Supporting Information

Oxidative cyclization of alkenoic acids with AgOAc

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General Information

All reactions (except the hydrolysis of esthers 1c-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\textsubscript{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 °C 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 polyethylene 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.

![Scheme 1](image1)

**Scheme 1.**

![Scheme 2](image2)

**Scheme 2.**
The following compounds were purchased from Aldrich and used as received:

Salicylic acid, 4-methoxysalicylic 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-naphthalene-carboxylic 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$_2$SO$_4$ (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$_2$CO$_3$ 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$_2$SO$_4$ 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, SOCl₂ (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 SOCl₂ were removed under vacuum. The residue obtained was dissolved in DCM and a saturated solution of NaHCO₃ (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 Na₂SO₄ 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

![Methylsalicylate (Ib)](image)

Method A. Colorless oil, (4.04 g, 92%). ¹H NMR (300 MHz, CDCl₃) 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

![Methyl 4-methoxysalicylate (IIb)](image)

Method A. White solid, (2.655 g, 98%). ¹H NMR (300 MHz, CDCl₃) 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

![Methyl 4-chlorosalicylate (IIIb)](image)

Method A. Pink oil, (2.12 g, 98%). ¹H NMR (300 MHz, CDCl₃) 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). ¹³C NMR (75 MHz, CDCl₃) δ 170.12 (C), 162.23 (C), 141.56 (C), 131.01 (CH), 120.00 (CH), 117.86 (CH), 111.11 (C), 52.60 (CH₃).

**Methyl 3-methylsalicylate (IVb).**⁴

![Methyl 3-methylsalicylate (IVb)](image)
Method A. Yellow oil, (4.47 g, 68%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 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):**

\[
\begin{align*}
\text{MeO} & \quad \text{O} \\
\text{OH} & \quad \text{OH}
\end{align*}
\]

Method A. Yellowish oil, (0.42 g, 96%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 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):**

\[
\begin{align*}
\text{Cl} & \quad \text{O} \\
\text{Me} & \quad \text{OH}
\end{align*}
\]

Method A. White solid, (4.67 g, 87%). \(^1\)H NMR (301 MHz, CDCl\(_3\)) \(\delta\) 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):**

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{O} \\
\text{Me} & \quad \text{OH}
\end{align*}
\]

Method A. White solid, (0.30 g, 71%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 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-4H-1,3-benzodioxin-4-one (VIIIb):**

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{OH} & \quad \text{OH}
\end{align*}
\]

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 °C and a solution of SOCl\(_2\) (0.34 mL, 4.61 mmol) in ether (0.5 mL) was added dropwise 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\(_3\)) \(\delta\) 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).\(^9\)

![Structure of Methyl 1-hydroxy-2-naphthoate (IXb)](image)

Method B (reaction time: 48 h). Light yellow solid, (1.117 g, 35%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 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).\(^10\)

![Structure of Methyl Anthranilate (Xb)](image)

Method B. Yellowish oil, (2.87 g, 95%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 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\(_2\)CO\(_3\) (20 mmol) and the allylic bromide or bencyl bromide (12.8 mmol) was stirred in DMF at 25 °C 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\(_2\)SO\(_4\) 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).**\(^11\)

![Structure of Methyl 2-allyloxy-benzoate (Ic)](image)

Yellowish oil, (0.448 g, 99%). \(^1\)H RMN (300 MHz, CDCl\(_3\)) \(\delta\) 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):**\(^12\)

![Structure of Methyl 2-allyloxy-4-methoxybenzoate (IIc)](image)

Yellowish oil, (0.23 g, 64%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 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):\(^3\)

\[
\begin{array}{c}
\text{Cl} \\
\text{O} \\
\text{Me}
\end{array}
\]

Yellowish solid, (0.14 g, 87%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 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, CDCl\(_3\)) \(\delta\) 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):\(^{13}\)

\[
\begin{array}{c}
\text{Me}
\end{array}
\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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):\(^{14}\)

\[
\begin{array}{c}
\text{MeO} \\
\text{O} \\
\text{Me}
\end{array}
\]

Yellowish oil, (0.242 g, 99%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 166.71 (C), 153.45 (C), 152.54 (C), 132.89 (CH), 121.41 (C), 119.70 (CH), 117.41 (CH\(_2\)), 115.16 (CH\(_2\)), 75.02 (CH\(_2\)), 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):\(^3\)

\[
\begin{array}{c}
\text{Cl} \\
\text{O} \\
\text{Me}
\end{array}
\]

Pink oil, (0.447 g, 98%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 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,
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).

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.

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

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, $J = 8.5$, 9.0 Hz, 1H), 6.54 (dd, $J = 8.2$, 9.0 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):

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):

\[
\begin{align*}
\text{O} & \quad \text{Me} \\
\text{N} & \quad \text{Os} \\
\end{align*}
\]

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

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 °C for 1 h before a solution of 4-methylbenzene-1-sulfonyl chloride (2.27 g, 11.91 mmol) in DCM (8 mL) was slowly added. After stirring the reaction mixture at 25 °C for 24 h a saturated aqueous solution of NH\(_4\)Cl was added. The organic phase was extracted with DCM (4 x 30 mL) dried over Na\(_2\)SO\(_4\) 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\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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\(_4\)S \([\text{M+H}]^+\): 346.11130; found: 346.11174.

Methyl 2-\{(1-methyl-2-propen-1-yl)oxy\}-benzoate (Xlc):

\[
\begin{align*}
\text{O} & \quad \text{Me} \\
\end{align*}
\]

Synthesis of but-3-en-2-yl methanesulfonate:

To a solution of but-3-en-2-ol (13.86 mmol) and Et\(_3\)N (20.8 mmol) in DCM (40 mL), was was added dropwise MeSO\(_2\)Cl (17.33 mmol) at 0 °C. The mixture was stirred at the same
temperature for 2 h. Then a saturated solution of Na₂CO₃ (21 ml) was added to quench the reaction. After the separation of the organic layer, the aqueous layer was extracted with DCM (4 x 20 mL). The combined organic layer was dried with anhydrous Na₂SO₄ 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), K₂CO₃ (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 Na₂SO₄ 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, CDCl₃) 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). IR (neat): 2982, 2950, 1728, 1599, 1581, 1486 cm⁻¹. HRMS-DART calculated for C₇H₉O₃ [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, CDCl₃) 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). ¹³C NMR (100 MHz, CDCl₃) 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 (CH₂), 52.24 (CH₃), 43.87 (CH), 20.30 (CH₃). IR (neat): 2951, 2925, 1712, 1461, 1433, 1285 cm⁻¹. HRMS-DART calculated for C₁₂H₁₅O₃S₁ [M+H]^+ : 223.07927; found: 223.07937.

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

Yellow solid. Obtained: 0.487 g (92%). ¹H NMR (300 MHz, CDCl₃) 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):

\[ \text{Colorless oil, (0.579 g, 80%).} \]
\[ \text{\( ^1 \)H NMR (400 MHz, CDCl}_3 \text{)} \delta 7.80 – 7.77 (m, 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). \]
\[ \text{\( ^13 \)C NMR (100 MHz, CDCl}_3 \text{)} \delta 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). \]
\[ \text{IR (neat): 2947, 2916, 1728, 1598, 1488, 1449 cm}^{-1}. \]
\[ \text{HRMS-DART calculated for C\textsubscript{13}H\textsubscript{17}O\textsubscript{3} [M+H]^+: 221.11777; found: 221.11841.} \]

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

\[ \text{Colorless oil, (0.34 g, 94%).} \]
\[ \text{\( ^1 \)H NMR (500 MHz, CDCl}_3 \text{)} \delta 7.83 – 7.81 (m, 1H), 7.54 – 7.24 (m, 4H), 7.03 – 6.97 (m, 2H), 5.19 (s, 2H), 3.91 (s, 3H). \]
\[ \text{\( ^{13} \)C NMR (125 MHz, CDCl}_3 \text{)} \delta 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\_2), 49.55 (CH\_2), 25.81 (CH\_3), 21.65 (CH\_3), 17.67 (CH\_3). \]
\[ \text{IR (neat): 2947, 2919, 1725, 1597, 1489 cm}^{-1}. \]
\[ \text{HRMS-DART calculated for C\textsubscript{20}H\textsubscript{24}NO\textsubscript{4}S [M+H]^+: 374.14260; found: 374.14377.} \]

Methyl 2-benzyloxy-benzoate (XIb):

\[ \text{White solid, (0.80 g, 73%).} \]
\[ \text{\( ^1 \)H NMR (300 MHz, CDCl}_3 \text{)} \delta 7.83 – 7.81 (m, 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):

\[ \text{White solid, (0.80 g, 73%).} \]
\[ \text{\( ^1 \)H NMR (300 MHz, CDCl}_3 \text{)} \delta 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). \]
To a solution of Et₂Zn22 (3.12 mL, 1 M in hexane) in freshly distilled CH₂Cl₂ (4 mL) at 0 °C was slowly added a solution of CF₃CO₂H (0.24 mL, 3.12 mmol mmol) in DCM (2 mL). Upon stirring for 20 min, a solution of CH₂I₂ (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 NH₄Cl, 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 Na₂SO₄ 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, CDCl₃) 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). ¹³C NMR (75 MHz, CDCl₃) δ 167.04 (C), 158.72 (C), 133.40 (CH), 131.69 (CH), 120.99 (C), 120.43 (CH), 114.25 (CH), 73.63 (CH₃), 52.03 (CH₂), 10.31 (CH₂), 3.16 (CH). IR (neat): 3006, 2949, 2873, 1727, 1707, 1599, 1489 cm⁻¹. HRMS-FAB calculated for C₁₂H₁₄O₃[M+H]+: 207.1021; found: 207.1022.

Synthesis of alkenoic acids 1a-21a:

Method A:

To a solution of the corresponding ester (2.62 mmol) in EtOH (20 mL) a saturated aqueous solution of KOH (30 drops) was added. The homogeneous mixture was stirred at 25 °C 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 Na₂SO₄ 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 °C was added water (1.5 mmol). After stirring for 10 minutes, a solution of the corresponding ester (0.50 mmol) in DMF (3 mL) was added to the suspension. The reaction mixture was stirred from 0 °C to 25 °C until the ester was totally consumed, then HCl 10% was added until pH = 2. The organic phase was extracted with Et₂O (3 x 20 mL) and the combined organic phases were dried over Na₂SO₄ and concentrated under vacuum. If necessary, the final alkenoic acids were further purified washing with pentane.

Method C:

To a solution of LiOH·H₂O (0.083 g, 1.99 mmol) in THF:H₂O (1:1, 4 mL) at 0 °C was added H₂O₂ (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 °C to 25 °C until the ester was totally consumed. Thereafter a solution of Na₂SO₃ (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 Na₂SO₄ and concentrated under vacuum. If necessary, the final alkynoic acids were further purified washing with pentane or by column chromatography.
2-Allyloxybenzoic acid (1a):$^{23}$

\[
\begin{align*}
\text{Method A. White solid, (0.99 g, 99%). } & \quad \text{\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) } \delta 9.81 \text{ (br s, 1H), 8.16 (dd, } J = 7.8, 1.8 \text{ Hz, 1H), 7.53 (ddd, } J = 8.5, 7.4, 1.8 \text{ Hz, 1H), 7.12 (dt, } J = 7.8, 1.1 \text{ Hz, 1H), 7.04 (d, } J = 8.4 \text{ Hz, 1H), 6.08 (ddt, } J = 17.2, 10.5, 5.6 \text{ Hz, 1H), 5.48 (dq, } J = 17.2, 1.4 \text{ Hz, 1H), 5.42 (dq, } J = 10.5, 1.1 \text{ Hz, 1H), 4.78 (dt, } J = 5.6, 1.3 \text{ Hz, 2H).}
\end{align*}
\]

2-Allyloxy-4-methoxybenzoic acid (2a):$^{24}$

\[
\begin{align*}
\text{Method A. White solid, (0.05 g, 36%). } & \quad \text{\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) } \delta 10.73 \text{ (br s, 1H), 8.11 (d, } J = 8.8 \text{ Hz, 1H), 6.63 (dd, } J = 8.8, 2.3 \text{ Hz, 1H), 6.51 (d, } J = 2.3 \text{ Hz, 1H), 6.08 (ddt, } J = 17.2, 10.4, 5.6 \text{ Hz, 1H), 5.48 (dq, } J = 17.3, 1.5 \text{ Hz, 1H), 5.42 (dq, } J = 10.5, 1.1 \text{ Hz, 1H), 4.75 (dt, } J = 5.6, 1.3 \text{ Hz, 2H), 3.85 (s, 3H).}
\end{align*}
\]

2-Allyloxy-4-chlorobenzoic acid (3a):$^{25}$

\[
\begin{align*}
\text{Method A. White solid, (0.08, 75%). } & \quad \text{\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) } \delta 10.70 \text{ (br s, 1H), 8.11 (d, } J = 8.4 \text{ Hz, 1H), 7.12 (dd, } J = 8.4, 1.8 \text{ Hz, 1H), 7.04 (d, } J = 1.9 \text{ Hz, 1H), 6.08 (ddt, } J = 17.2, 10.4, 5.6 \text{ Hz, 1H), 5.56 – 5.44 (m, 2H), 4.78 (dt, } J = 5.6, 1.2 \text{ Hz, 2H).}
\end{align*}
\]

2-Allyloxy-3-methylbenzoic acid (4a):$^{12}$

\[
\begin{align*}
\text{Method A. White solid, (0.43 g, 96%). } & \quad \text{\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) } \delta 11.16 \text{ (br s, 1H), 7.99 – 7.94 (m, 1H), 7.47 – 7.40 (m, 1H), 7.19 (t, } J = 7.7 \text{ Hz, 1H), 6.11 (ddt, } J = 17.1, 10.3, 6.0 \text{ Hz, 1H), 5.47 (dq, } J = 17.1, 1.4 \text{ Hz, 1H), 5.39 (dq, } J = 10.3, 1.1 \text{ Hz, 1H), 4.51 (ddd, } J = 6.0, 1.4, 1.0 \text{ Hz, 2H), 2.37 (s, 3H).}
\end{align*}
\]
2-Allyloxy-5-methoxybenzoic acid (5a):\textsuperscript{21}

\[
\begin{array}{c}
\text{MeO} \\
\chem{\text{O}} \\
\text{OH} \\
\text{\chem{\text{O}}-\text{CH}=\text{CH}_2}
\end{array}
\]

Method A. White solid, (0.18 g, 70%). \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 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):\textsuperscript{21}

\[
\begin{array}{c}
\text{Cl} \\
\chem{\text{O}} \\
\text{OH} \\
\text{\chem{\text{O}}-\text{CH}=\text{CH}_2}
\end{array}
\]

Method A. White solid, (0.43, 96%). \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 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):

\[
\begin{array}{c}
\text{O}_2\text{N} \\
\chem{\text{O}} \\
\text{OH} \\
\text{\chem{\text{O}}-\text{CH}=\text{CH}_2}
\end{array}
\]

Method A. Orange solid, (0.10 g, 99%), mp = 134-135 °C. \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 165.78 (C), 162.48 (C), 140.63 (C), 135.66 (CH), 130.62 (CH), 121.37 (CH\textsubscript{2}), 112.60 (CH), 102.66 (CH), 102.02 (C), 71.40 (CH\textsubscript{2}). IR (neat): 3417, 1709, 1619, 1528, 1457 cm\textsuperscript{-1}. HRMS-DART calculated for C\textsubscript{10}H\textsubscript{10}NO\textsubscript{5} [M+H]\textsuperscript{+}: 224.05590; found: 224.05566.

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

\[
\begin{array}{c}
\text{OH} \\
\text{\chem{\text{O}}-\text{CH}=\text{CH}_2}
\end{array}
\]

Method B. Pinkish solid, (0.22 gr, 87%), m.p.: 41-43 °C. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 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). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 170.95 (C), 164.41 (C), 157.72 (C), 135.66 (CH), 130.62 (CH), 121.37 (CH\textsubscript{2}), 112.60 (CH), 102.66 (CH), 102.02 (C), 71.40 (CH\textsubscript{2}). IR (neat): 3214, 2883, 1688, 1619, 1528, 1457 cm\textsuperscript{-1}. HRMS-DART calculated for C\textsubscript{10}H\textsubscript{11}O\textsubscript{4} [M+H]\textsuperscript{+}: 195.06573; found: 195.06536.
1-Allyloxy-2-naphtoic acid (9a):[^25]

![Chemical Structure of 1-Allyloxy-2-naphtoic Acid](image)

Method A. White solid, (0.29 g, 99%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 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):[^26]

![Chemical Structure of 2-Allylthio-benzoic Acid](image)

A mixture of 2-thiosalicylic (0.20 g, 1.29 mmol), K$_2$CO$_3$ (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$_4$Cl 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$_2$SO$_4$ and concentrated under vaccum. The white solid obtained was purified washing with pentane, (0.18 g, 73%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 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 (dd, $J = 7.9$, 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):[^27]

![Chemical Structure of 2-[(4-Methylphenyl)sulfonyl]-2-propen-1-ylamino}benzoic Acid](image)

Method B. Yellow solid, (0.32 g, 96%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 165.60 (C), 156.70 (C), 136.84 (CH), 134.89 (CH), 133.79 (CH), 122.48 (CH), 118.54 (C), 118.10 (CH), 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):

$$\begin{array}{c}
\text{O} \\
\text{S} \\
\text{CH}_2
\end{array}$$

Method C. White solid, (0.15 g, 81%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_2$S [M+H]+: 209.06362; found: 209.06349.

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

$$\begin{array}{c}
\text{O} \\
\text{C} \\
\text{C}
\end{array}$$

Method A. Yellowish solid, (0.03 g, 35%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 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):

$$\begin{array}{c}
\text{O} \\
\text{C} \\
\text{CH}_3
\end{array}$$

Method A. White solid, (0.85 g, 76%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_4$S [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$_3$N (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$_4$Cl was added and the aqueous phase was extracted with DCM (3 x 5 mL). The combined organic phases were dried with anhydrous Na$_2$SO$_4$ 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$_3$) $\delta$ 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$_3$) $\delta$ 162.17 (C), 156.87 (C), 138.97 (C), 135.07 (C), 132.62 (CH), 132.04 (CH), 130.00 (CH), 129.62 (CH), 128.15 (CH), 117.54 (CH), 49.69 (CH$_2$), 25.65 (CH$_3$), 21.60 (CH$_3$), 17.58 (CH$_3$). IR (neat): 3288, 3245, 3096, 1680, 1589 cm$^{-1}$. HRMS-DART calculated for C$_{16}$H$_{16}$NO$_4$S [M+H]$^+$: 318.08000; found: 318.08070.

Allyl phenyl ether (18a):
A mixture of phenol (1.00 gr, 10.62 mmol), K₂CO₃ (2.93 gr, 21.24 mmol) and allyl bromide (1.10 mL, 12.7 mmol) was stirred in DMF (27 mL) at 70 °C 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 Na₂SO₄ and concentrated under vacuum. The residue obtained was further purified by silica gel chromatography (hexane/EtOAc, 100:1).

Yellowish oil, (0.435 g, 31 %) ¹H NMR (300 MHz, CDCl₃) 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-Benzylxoy-benzoic acid (19a):¹

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Method A. White solid, (0.52 g, 88%). ¹H NMR (300 MHz, CDCl₃) 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

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\text{O} \backslash \text{O} \backslash \text{O} \backslash \text{C} \text{O}
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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 °C. After stirring for 10 min, methyl acrilate (1.04 mL, 11.61 mmol) was added at 0 °C. The mixture was stirred from 0 °C to 25 °C 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 mixture 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 °C 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 Na₂SO₄ and concentrated under vacuum.

Yellowish oil (0.19 g, 13%). ¹H NMR (300 MHz, CDCl₃) 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

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\text{O} \backslash \text{O} \backslash \text{O} \backslash \text{C} \text{O}
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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 °C for 18 h. After cooling to rt, a saturated solution of NH$_4$Cl (5 mL) was added, and the mixture was extracted with DCE (3 x 5 mL). The combined organic phases were dried with anhydrous Na$_2$SO$_4$ 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):$^1$

![2-Ethenyl-4H-1,3-benzodioxin-4-one (1b)](image)

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), 3.88 (s, 3H). $^{13}$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, 2946, 2843, 1733, 1612, 1587 cm$^{-1}$. HRMS-DART calculated for C$_{10}$H$_9$O$_3$ [M+H]$^+$: 177.05517; found: 177.05562.

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

![2-Ethenyl-7-methoxy-4H-1,3-benzodioxin-4-one (2b)](image)

Yellowish oil, (0.013 g, 44%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.91 (d, $J = 8.8$ Hz, 1H), 6.73 (ddd, $J = 8.8, 2.4$ 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$_3$) $\delta$ 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$_3$) $\delta$ 160.99 (C), 158.42 (C), 142.56 (C), 131.49 (CH), 130.43 (CH), 124.48 (CH), 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$_8$ClO$_3$ [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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$ [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$_3$) $\delta$ 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$_3$) $\delta$ 160.67 (C), 156.50 (C), 136.52 (CH), 207.06573; found: 207.06612.
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$_8$ClO$_3$ [M+H]$^+$: 211.01620; found: 211.01663.

4-Allyloxy-1-chlorobenzene (6c).$^{32}$

\[
\begin{align*}
\text{Cl} & \quad \text{O} \quad \text{CH}_{2} \quad \text{CH} \\
\end{align*}
\]

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 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).$^{33}$

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{O} \quad \text{CH}_{2} \quad \text{CH} \\
\end{align*}
\]

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 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-4H-1,3-benzodioxin-4-one (8b):

\[
\begin{align*}
\text{O} & \quad \text{O} \quad \text{CH}_{2} \quad \text{CH} \\
\end{align*}
\]

Yellowish oil, (0.002 g, 4 %). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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 (dd, $J = 17.1$, 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$_3$) $\delta$ 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):$^{34}$

\[
\begin{align*}
\text{O} & \quad \text{O} \quad \text{CH}_{2} \quad \text{CH} \\
\end{align*}
\]

Yellowish oil, (0.003 g, 7 %). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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-4H-naphtho[1,2-d][1,3]dioxin-4-one (9b):

Yellowish oil, (0.05 g, 50%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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-4H-3,1-benzoxathiin-4-one (10b):

Pink oil, (0.025 g, 84%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_9$O$_2$S [M+H]$^+$: 193.03232; found: 193.03262.

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

Yellowish oil, (0.013 g, 67%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_4$S [M+H]$^+$: 330.08000; found: 330.08084.
2-Ethenyl-2-methyl-4H-1,3-benzodioxin-4-one (12b):\textsuperscript{35}

![Structure of 2-Ethenyl-2-methyl-4H-1,3-benzodioxin-4-one (12b)](image)

Yellowish oil, (0.015 g, 20%) \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 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). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 161.52 (C), 156.38 (C), 136.56 (C), 136.43 (CH), 129.77 (CH), 122.89 (CH), 119.78 (CH\textsubscript{2}), 117.09 (CH), 114.63 (C), 105.33 (CH), 26.82 (CH\textsubscript{3}). IR (neat): 3086, 2920, 2852, 1746, 1613, 1592 cm\textsuperscript{-1}. HRMS-DART calculated for C\textsubscript{11}H\textsubscript{11}O\textsubscript{3} [M+H]\textsuperscript{+}: 191.07082; found: 191.07091.

2-Ethenyl-2-methyl-4H-1,3-benzoxathiin-4-one (13b):\textsuperscript{38}

![Structure of 2-Ethenyl-2-methyl-4H-1,3-benzoxathiin-4-one (13b)](image)

Yellowish (0.019 g, 47%) \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 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). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 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\textsubscript{2}), 87.34 (C), 28.20 (CH\textsubscript{3}). IR (neat): 3066, 2986, 2927, 2852, 1719, 1589, 1440 cm\textsuperscript{-1}. HRMS-DART calculated for C\textsubscript{11}H\textsubscript{11}O\textsubscript{2}S [M+H]\textsuperscript{+}: 207.04797; found: 207.04800.

Cinnamyloxybenzene (14c).\textsuperscript{36}

![Structure of Cinnamyloxybenzene (14c)](image)

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 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).\textsuperscript{37}

![Structure of Benzyloxybenzene (19c)](image)

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 7.50 – 7.27 (m, 7H), 7.08 – 6.95 (m, 3H), 5.08 (s, 2H).

\textsuperscript{2} M.-C. Matos, P. V. Murphy, \textit{J. Org. Chem.}, 2007, 72, 1803-1806.


