

## Tetrahydropyranylation of Alcohols and Phenols by Using Simple Simple and Inexpensive Organocatalyst

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**Abstract:** A simple and convenient procedure for tetrahydropyranylation of alcohols and phenols in the presence of organocatalyst, 3,5-dinitrobenzoic acid, has been developed. 3,5-Dinitrobenzoic acid is an effective, very cheap and viable catalyst in above synthetic transformations with various alcohols, phenols. A large number of alcohols and phenols have been tolerated well in this protocol.

**Keywords:** Organocatalyst, 3,5-Dinitrobenzoic acid, Tetrahydropyranylation, alcohols, phenols.

### I. Introduction

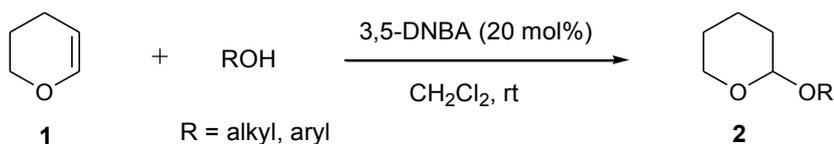
The choice of the protection and deprotection strategy in a synthetic series is inevitable, owing to chemoselective transformations in the presence of various functional groups. The tetrahydropyranyl ethers (THP ethers) are attractive because of low cost of 3,4-dihydro-2H-pyran (DHP) and stability of THP derivatives towards various reaction conditions such as strong bases, Grignard reagents, hydrides, redox reagents, alkylating, acylating agents and catalytic hydrogenation and easy removal under mild acidic conditions. This transformation is generally achieved using both protonic as well as Lewis acid catalysts. Consequently a variety of reagents such as pTSA,<sup>2</sup> BF<sub>3</sub>.OEt<sub>2</sub>,<sup>3</sup> ZnCl<sub>2</sub> impregnated alumina,<sup>4</sup> TBATB,<sup>5</sup> PPTS,<sup>6</sup> acetyltriphenylphosphonium bromide,<sup>7</sup> aluminum chloride hexahydrate,<sup>8</sup> In(OTf)<sub>3</sub>,<sup>9</sup> Bi(OTf)<sub>3</sub>,<sup>10</sup> LiOTf,<sup>11</sup> dialkylimidazolium tetrachloroaluminates,<sup>12</sup> InCl<sub>3</sub> immobilized in ionic liquids,<sup>13</sup> bromodimethylsulfonium bromide,<sup>14</sup> cupric sulfate pentahydrate,<sup>15</sup> CAN,<sup>16</sup> and bismuth(III) nitrate pentahydrate<sup>17</sup> and photosensitization<sup>18</sup> have been introduced for tetrahydropyranyl protection of alcohols and phenols. However, some of these procedures suffer due to the use of expensive and moisture sensitive catalysts, high temperature, longer reaction times and incompatibility with other functional groups, and some reagents also have to be freshly prepared prior to use.<sup>6,8,11,15</sup> Though metal triflates have been found to be effective catalysts for tetrahydropyranylation, these reagents have limited applicability since they are relatively expensive, difficult to handle, and not readily available. Furthermore, the procedures involving these reagents require harsh and inert reaction conditions.

### II. Results and Discussions

With an objective of developing a viable procedure for tetrahydropyranylation, we focused on finding a cheap and efficient catalyst that would give high yields and easy handling procedure under aerobic conditions. In continuation of our work on novel organocatalysts for organic transformations, we became interested to use very cheap 3,5-dinitrobenzoic acid (3,5-DNBA, <\$0.1 per gram) as organocatalyst for the aforementioned reaction. Though 3,5-DNBA has been used as an additive in many reactions,<sup>19</sup> it has not been used as a catalyst. In this paper, we describe the successful implementation of 3,5-DNBA as an organocatalyst for the tetrahydropyranylation of various primary and secondary alcohols and phenols.

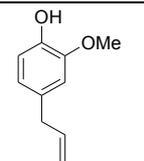
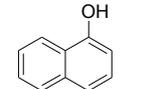
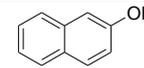


Initially, the tetrahydropyranylation of phenol (1 mmol) was performed with DHP (1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) in the presence of 20 mol% 3,5-DNBA at room temperature under aerobic conditions (Table 1, Entry 7). As a result the transformation took place in 3 h to afford its tetrahydropyranyl ether **2g** in 88% yield. We have also performed the reaction with 10 mol% catalyst but the reaction was completed in 11 h with 85% yield of **2g**. Using the protocol, various primary, secondary alcohols and phenols were transformed easily into the corresponding THP-ethers in good yields (Table 1). It is observed that phenols bearing electron withdrawing substituents gave protected THP-ethers in good yields (Table 1, Entry 14). Importantly, no isomerization of double bond took place in case of eugenol (Table 1, Entry 16).



**Table 1.** Tetrahydropyranylation of alcohols and phenols catalyzed by 3,5-dinitrobenzoic acid.<sup>a</sup>

Entry	Substrate (ROH)	Time (h)	Product (ROTHP)	Yield <sup>b</sup> (%)
1		2	<b>2a</b>	91
2		2	<b>2b</b>	91
3		2	<b>2c</b>	92
4		2	<b>2d</b>	94
5		2	<b>2e</b>	97
6		2	<b>2f</b>	98
7		3	<b>2g</b>	88
8		6	<b>2h</b>	80
9		8	<b>2i</b>	86
10		4	<b>2j</b>	91
11		4	<b>2k</b>	82
12		4	<b>2l</b>	91
13		3	<b>2m</b>	85
14		8	<b>2n</b>	84
15		8	<b>2o</b>	80

16		8	2p	81
17		4	2q	81
18		4	2r	87

<sup>a</sup>The reactions were carried out with 1 mmol of alcohol/phenol and 1 mmol of DHP in presence of 0.2 mmol (20 mol%) of 3,5-DNBA at room temperature. <sup>b</sup>Yields are of pure and isolated products.

### III. Conclusion

In conclusion, we have developed a simple and convenient method for tetrahydropyranylation of alcohols and phenols in the presence of 3,5-dinitrobenzoic acid. 3,5-dinitrobenzoic acid is an effective, very cheap and viable catalyst in above synthetic transformations with various alcohols, phenols. We believe that this methodology is valuable addition to modern synthetic methodologies.

### IV. Experimental

#### General procedure for the synthesis of tetrahydropyranyl ethers

A solution of an alcohol or a phenol (1 mmol), dihydro-2H-pyran (DHP, 1 mmol), and 3,5-dinitrobenzoic acid (3,5-DNBA, 0.2 mmol, 20 mol%), in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) were stirred at ambient temperature for an appropriate time (monitored by TLC or GC). After completion of the reaction (45 min for alcohols and 3 h for phenols), the organic layer was washed twice with 10 mL of saturated NaHCO<sub>3</sub> solution, dried (anhyd. Na<sub>2</sub>SO<sub>4</sub>), and concentrated under reduced pressure to yield almost pure product. The product was purified further by column chromatography on silica gel using ethyl acetate/hexanes as the eluent (1:9).

#### Prop-2-enyl tetrahydro-2H-pyran-2-yl ether (2a):

**Reaction time:** 45 min.

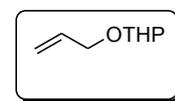
**Yield:** 0.131 g (92%) as colourless oily liquid.

**IR (neat)  $\nu_{\max}$ :** 3065, 2956, 2834, 1457, 1025, 1014 cm<sup>-1</sup>.

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):**  $\delta$  5.97-5.89 (m, 1H), 5.30-5.26 (m, 1H), 5.15 (d, J = 10.5 Hz, 1H), 4.63 (t, J = 3 Hz, 1H), 4.24-4.21 (m, 1H), 3.99-3.95 (m, 1H), 3.88-3.84 (m, 1H), 3.51-3.47 (m, 1H), 1.85-1.81 (m, 1H), 1.74-1.68 (m, 1H), 1.62-1.50 (m, 4H) ppm.

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):**  $\delta$  135.1, 117.0, 98.3, 68.3, 62.5, 31.0, 25.9, 19.8 ppm.

**MS:** m/z = 142 [M<sup>+</sup>].



#### Propyl tetrahydro-2H-pyran-2-yl ether (2b):

**Reaction time:** 45 min.

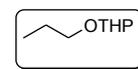
**Yield:** 0.133 g (93%) as colourless oily liquid.

**IR (neat)  $\nu_{\max}$ :** 2943, 2854, 1457, 1336, 1101, 1056 cm<sup>-1</sup>.

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):**  $\delta$  4.55 (t, J = 3.5 Hz, 1H), 3.86-3.82 (m, 1H), 3.68-3.64 (m, 1H), 3.48-3.45 (m, 1H), 3.35-3.30 (m, 1H), 1.82-1.79 (m, 1H), 1.70-1.66 (m, 1H), 1.61-1.48 (m, 6H), 0.90 (t, J = 7.5 Hz, 3H) ppm.

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):**  $\delta$  98.8, 69.2, 62.3, 30.7, 25.4, 22.9, 19.6, 10.6 ppm.

**MS:** m/z = 145 [M + H]<sup>+</sup>.



#### Butyl tetrahydro-2H-pyran-2-yl ether (2c):

**Reaction time:** 45 min.

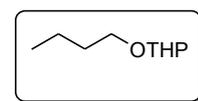
**Yield:** 0.146 g (93%) as colourless oily liquid.

**IR (neat)  $\nu_{\max}$ :** 2946, 2853, 1452, 1365, 1152, 1065 cm<sup>-1</sup>.

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):**  $\delta$  4.50 (t, J = 3.5 Hz, 1H), 3.81-3.77 (m, 1H), 3.69-3.64 (m, 1H), 3.44-3.41 (m, 1H), 3.33-3.29 (m, 1H), 1.77-1.75 (m, 1H), 1.65-1.61 (m, 1H), 1.52-1.43 (m, 6H), 1.34-1.30 (m, 2H), 0.86 (t, J = 7.5 Hz, 3H) ppm.

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):**  $\delta$  99.1, 67.7, 62.6, 32.2, 31.1, 25.9, 20.0, 19.8, 14.2 ppm.

**MS:** m/z = 158 [M<sup>+</sup>].



**Cyclohexyl tetrahydro-2H-pyran-2-yl ether (2d):**

**Reaction time:** 45 min.

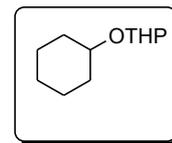
**Yield:** 0.173 g (94%) as colourless oily liquid.

**IR (neat)  $\nu_{\max}$ :** 2932, 2858, 1451, 1354, 1125, 1068  $\text{cm}^{-1}$ .

**$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz):**  $\delta$  4.72 (bs, 1H), 3.93-3.87 (m, 1H), 3.63-3.59 (m, 1H), 3.50-3.47 (m, 1H), 1.91-1.84 (m, 3H), 1.75-1.70 (m, 3H), 1.55-1.54 (m, 5H), 1.40-1.18 (m, 5H) ppm.

**$^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz):**  $\delta$  96.6, 74.4, 62.8, 33.7, 31.8, 31.3, 25.7, 25.5, 24.5, 24.2, 20.0 ppm.

**MS:**  $m/z = 184$  [ $\text{M}^+$ ].



**Benzyl tetrahydro-2H-pyran-2-yl ether (2e):**

**Reaction time:** 45 min.

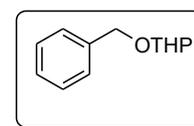
**Yield:** 0.184 g (96%) as colourless oily liquid.

**IR (neat)  $\nu_{\max}$ :** 3052, 2948, 1675, 1594, 964, 850, 742  $\text{cm}^{-1}$ .

**$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz):**  $\delta$  7.36-7.31 (m, 4H), 7.28-7.25 (m, 1H), 4.78 (d,  $J = 12.0$  Hz, 1H), 4.70 (t,  $J = 3.5$  Hz, 1H), 4.49 (d,  $J = 12.0$  Hz, 1H), 3.93-3.89 (m, 1H), 3.56-3.51 (m, 1H), 1.87-1.85 (m, 1H), 1.73-1.50 (m, 5H) ppm.

**$^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz):**  $\delta$  138.3, 128.3, 127.8, 127.5, 97.7, 68.8, 62.1, 30.6, 25.5, 19.4 ppm.

**MS:**  $m/z = 193$  [ $\text{M} + \text{H}$ ] $^+$ .



**3-Phenyl-2-propenyl tetrahydro-2H-pyran-2-yl ether (2f):**

**Reaction time:** 45 min.

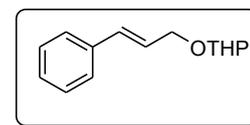
**Yield:** 0.207 g (95%) as colourless oily liquid.

**IR (neat)  $\nu_{\max}$ :** 3055, 3023, 2943, 1593, 1119, 984, 755  $\text{cm}^{-1}$ .

**$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz):**  $\delta$  7.38 (d,  $J = 8.0$  Hz, 2H), 7.29 (t,  $J = 8.0$  Hz, 2H), 7.22 (t,  $J = 8.0$  Hz, 1H), 6.61 (d,  $J = 8.0$  Hz, 1H), 6.33-6.28 (m, 1H), 4.70 (t,  $J = 3.5$  Hz, 1H), 4.41-4.37 (m, 1H), 4.17-4.13 (m, 1H), 3.92-3.88 (m, 1H), 3.55-3.50 (m, 1H), 1.87-1.85 (m, 1H), 1.76-1.72 (m, 1H), 1.66-1.51 (m, 4H) ppm.

**$^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz):**  $\delta$  136.7, 132.1, 128.4, 127.4, 126.3, 125.9, 97.7, 67.5, 62.0, 30.5, 25.3, 19.3 ppm.

**MS:**  $m/z = 219$  [ $\text{M} + \text{H}$ ] $^+$ .



**Phenyl tetrahydro-2H-pyran-2-yl ether (2g):**

**Reaction time:** 3 h.

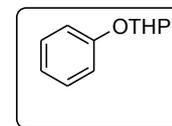
**Yield:** 0.170 g (96%) as colourless oily liquid.

**IR (neat)  $\nu_{\max}$ :** 3059, 2943, 1598, 1589, 964, 920, 754  $\text{cm}^{-1}$ .

**$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz):**  $\delta$  7.32-7.28 (m, 2H), 7.09-7.06 (m, 2H), 7.02-6.99 (m, 1H), 5.44 (t,  $J = 3.5$  Hz, 1H), 3.97-3.92 (m, 1H), 3.64-3.60 (m, 1H), 2.07-2.00 (m, 1H), 1.90-1.87 (m, 2H), 1.75-1.59 (m, 3H) ppm.

**$^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz):**  $\delta$  157.0, 129.3, 121.5, 116.4, 96.2, 61.9, 30.3, 25.1, 18.7 ppm.

**MS:**  $m/z = 179$  [ $\text{M} + \text{H}$ ] $^+$ .



**2-Methoxyphenyl tetrahydro-2H-pyran-2-yl ether (2h):**

**Reaction time:** 3 h.

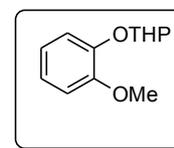
**Yield:** 0.191 g (92%) as colourless oily liquid.

**IR (neat)  $\nu_{\max}$ :** 3055, 2943, 1592, 1502, 1455, 872, 770  $\text{cm}^{-1}$ .

**$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz):**  $\delta$  7.02-6.99 (m, 2H), 6.84-6.82 (m, 2H), 5.29 (t,  $J = 3.5$  Hz, 1H), 3.97-3.92 (m, 1H), 3.76 (s, 3H), 3.61-3.58 (m, 1H), 2.02-1.98 (m, 1H), 1.87-1.83 (m, 2H), 1.69-1.60 (m, 3H) ppm.

**$^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz):**  $\delta$  154.9, 151.5, 118.2, 114.9, 97.7, 62.4, 56.0, 30.9, 25.7, 19.3 ppm.

**MS:**  $m/z = 209$  [ $\text{M} + \text{H}$ ] $^+$ .



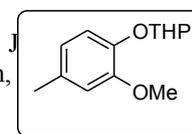
**2-Methoxy-4-methylphenyl tetrahydro-2H-pyran-2-yl ether (2i):**

**Reaction time:** 3 h.

**Yield:** 0.202 g (91%) as colourless oily liquid.

**IR (neat)  $\nu_{\max}$ :** 3035, 2941, 1590, 1511, 912, 871, 812  $\text{cm}^{-1}$ .

**$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz):**  $\delta$  7.01 (d,  $J = 8.0$  Hz, 1H), 6.72 (d,  $J = 1.5$  Hz, 1H), 6.69 (dt,  $J = 8.0, 1.0$  Hz, 1H), 5.33 (t,  $J = 3.0$  Hz, 1H), 4.05-4.00 (m, 1H), 3.84 (s, 3H), 3.60-3.57 (m, 1H), 2.30 (s, 3H), 2.03-2.01 (m, 1H), 1.94-1.93 (m, 1H), 1.90-1.87 (m, 1H), 1.69-1.60 (m, 3H) ppm.



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  150.1, 143.9, 132.3, 121.0, 118.2, 113.3, 97.8, 62.1, 55.9, 30.3, 25.2, 21.0, 18.8 ppm.

MS:  $m/z = 222$   $[\text{M}]^+$ .

#### 4-Bromophenyl tetrahydro-2H-pyran-2-yl ether (2j):

Reaction time: 3 h.

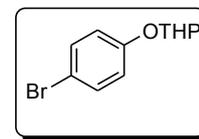
Yield: 0.241 g (94%) as colourless oily liquid.

IR (neat)  $\nu_{\text{max}}$ : 3064, 2943, 1589, 1578, 919, 823, 645  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.38-7.35 (m, 2H), 6.95-6.92 (m, 2H), 5.37 (t,  $J = 3.0$  Hz, 1H), 3.89-3.84 (m, 1H), 3.61-3.57 (m, 1H), 1.86-1.83 (m, 2H), 1.72-1.63 (m, 2H), 1.62-1.57 (m, 2H) ppm.

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  156.1, 132.1, 118.2, 113.7, 96.4, 61.9, 30.1, 25.0, 18.5 ppm.

MS:  $m/z = 258$   $[\text{M} + 2]^+$ .



#### 4-Chlorophenyl tetrahydro-2H-pyran-2-yl ether (2k):

Reaction time: 3 h.

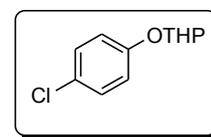
Yield: 0.191 g (90%) as colourless oily liquid.

IR (neat)  $\nu_{\text{max}}$ : 3076, 2944, 1596, 1583, 1489, 1021, 965, 919  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.22-7.19 (m, 2H), 6.99-6.96 (m, 2H), 5.34 (t,  $J = 3.0$  Hz, 1H), 3.88-3.83 (m, 1H), 3.60-3.56 (m, 1H), 2.00-1.95 (m, 1H), 1.86-1.82 (m, 2H), 1.68-1.56 (m, 3H) ppm.

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  156.1, 129.7, 126.9, 118.3, 97.1, 62.4, 30.7, 25.6, 19.1 ppm.

MS:  $m/z = 214$   $[\text{M} + 2]^+$ .



#### 4-Methoxyphenyl tetrahydro-2H-pyran-2-yl ether (2l):

Reaction time: 3 h.

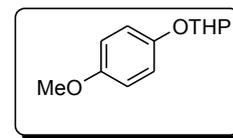
Yield: 0.199 g (96%) as colourless oily liquid.

IR (neat)  $\nu_{\text{max}}$ : 3039, 2943, 2872, 1506, 969, 920, 827  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.19 (dd,  $J = 8.0, 1.5$  Hz, 1H), 6.98-6.95 (m, 1H), 6.91-6.88 (m, 2H), 5.38 (t,  $J = 3.5$  Hz, 1H), 4.04-3.99 (m, 1H), 3.85 (s, 3H), 3.61-3.58 (m, 1H), 2.07-2.04 (m, 1H), 1.95-1.94 (m, 1H), 1.90-1.88 (m, 1H), 1.69-1.59 (m, 3H) ppm.

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  154.4, 151.0, 117.7, 114.4, 97.2, 61.9, 55.5, 30.4, 25.2, 18.8 ppm.

MS:  $m/z = 193$   $[\text{M} + \text{H}]^+$ .



#### 4-Methylphenyl tetrahydro-2H-pyran-2-yl ether (2m):

Reaction time: 3 h.

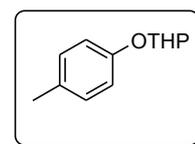
Yield: 0.180 g (94%) as colourless oily liquid.

IR (neat)  $\nu_{\text{max}}$ : 3027, 2942, 1609, 1585, 969, 920, 817  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.07-7.05 (m, 2H), 6.95-6.92 (m, 2H), 5.35 (t,  $J = 3.5$  Hz, 1H), 3.93-3.88 (m, 1H), 3.59-3.55 (m, 1H), 2.27 (s, 3H), 2.01-1.96 (m, 1H), 1.85-1.81 (m, 2H), 1.67-1.55 (m, 3H) ppm.

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  154.9, 130.8, 129.7, 116.4, 96.5, 61.9, 30.4, 25.2, 20.4, 18.8 ppm.

MS:  $m/z = 193$   $[\text{M} + \text{H}]^+$ .



#### 4-(Tetrahydro-2H-pyran-2-yloxy)benzaldehyde (2n):

Reaction time: 3 h.

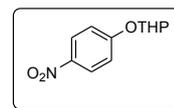
Yield: 0.187 g (91%) as colourless oily liquid.

IR (neat)  $\nu_{\text{max}}$ : 3050, 2947, 2756, 1669, 1602, 966, 834, 787  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  9.90 (s, 1H), 7.85-7.83 (m, 2H), 7.18-7.16 (m, 2H), 5.56 (t,  $J = 3$  Hz, 1H), 3.86 (td,  $J = 22.0, 11.0, 3.5$  Hz, 1H), 3.66-3.63 (m, 1H), 2.04-1.98 (m, 1H), 1.92-1.89 (m, 2H), 1.77-1.69 (m, 2H), 1.65-1.61 (m, 1H) ppm.

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  190.9, 162.1, 131.7, 130.4, 116.4, 96.0, 62.0, 30.0, 24.9, 18.3 ppm.

MS:  $m/z = 206$   $[\text{M}]^+$ .

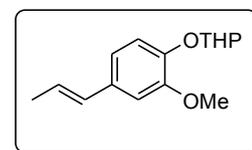


#### 2-Methoxy-4-(1-propenyl)phenyl tetrahydro-2H-pyran-2-yl ether (2o):

Reaction time: 3 h.

Yield: 0.225 g (91%) as colourless oily liquid.

IR (neat)  $\nu_{\text{max}}$ : 3045, 2950, 1600, 1591, 965, 927, 882  $\text{cm}^{-1}$ .



**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):** δ 6.95 (d, J = 8.5 Hz, 1H), 6.79 (bs, 1H), 6.74 (d, J = 8.0 Hz, 1H), 6.23 (d, J = 15.5 Hz, 1H), 6.05-5.98 (m, 1H), 5.27 (t, J = 3.0 Hz, 1H), 3.92-3.87 (m, 1H), 3.75 (d, J = 1.5 Hz, 3H), 3.50-3.47 (m, 1H), 1.98-1.91 (m, 1H), 1.85-1.83 (m, 1H), 1.76 (d, J = 6.5 Hz, 3H), 1.58-1.50 (m, 4H) ppm.

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):** δ 150.3, 145.4, 132.8, 130.7, 124.1, 118.7, 118.0, 109.8, 97.7, 62.1, 56.0, 30.3, 25.3, 18.8, 18.3 ppm.

HRMS (ESI) m/z Calcd for C<sub>15</sub>H<sub>21</sub>O<sub>3</sub> (M+H)<sup>+</sup>, 249.1491; Found, 249.1495.

**2-Methoxy-4-(2-propenyl)phenyl tetrahydro-2H-pyran-2-yl ether (2p):**

**Reaction time:** 3 h.

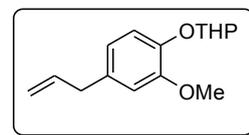
**Yield:** 0.233 g (94%) as colourless oily liquid.

**IR (neat) v<sub>max</sub>:** 3019, 2941, 1600, 1581, 962, 917, 871 cm<sup>-1</sup>.

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):** δ 7.05 (d, J = 8.0 Hz, 1H), 6.73 (d, J = 1.5 Hz, 1H), 6.70 (dd, J = 8.0, 1.5 Hz, 1H), 6.00-5.92 (m, 1H), 5.35 (t, J = 3.0 Hz, 1H), 5.11-5.05 (m, 2H), 4.04-3.99 (m, 1H), 3.83 (s, 3H), 3.60-3.57 (m, 1H), 3.33 (d, J = 6.5 Hz, 2H), 2.03-1.86 (m, 3H), 1.66-1.61 (m, 3H) ppm.

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):** δ 150.6, 144.9, 137.9, 134.8, 121.0, 118.5, 115.9, 113.2, 98.1, 62.4, 56.3, 40.2, 30.7, 25.6, 19.2 ppm.

**MS:** m/z = 248 [M]<sup>+</sup>.



**1-Naphthyl tetrahydro-2H-pyran-2-yl ether (2q):**

**Reaction time:** 3 h.

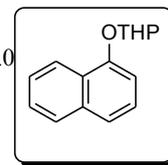
**Yield:** 0.221 g (97%) as colourless oily liquid.

**IR (neat) v<sub>max</sub>:** 3048, 2942, 1594, 1579, 958, 917, 872, 792 cm<sup>-1</sup>.

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):** δ 8.30-8.28 (m, 1H), 7.76-7.74 (m, 1H), 7.45-7.41 (m, 3H), 7.33 (t, J = 8.0 Hz, 1H), 7.11 (d, J = 8.0 Hz, 1H), 5.59 (t, J = 3.0 Hz, 1H), 3.90 (td, J = 7.0, 6.0, 3.0 Hz, 1H), 3.60-3.57 (m, 1H), 2.13-2.10 (m, 1H), 2.01-1.97 (m, 1H), 1.93-1.89 (m, 1H), 1.71-1.65 (m, 2H), 1.59-1.56 (m, 1H) ppm.

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):** δ 152.9, 135.0, 127.9, 126.5, 126.4, 126.4, 125.5, 122.3, 121.4, 108.6, 96.7, 62.2, 30.9, 25.6, 19.2 ppm.

**MS:** m/z = 229 [M]<sup>+</sup>.



**2-Naphthyl tetrahydro-2H-pyran-2-yl ether (2r):**

**Reaction time:** 3 h.

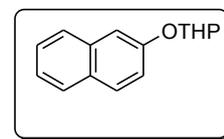
**Yield:** 0.216 g (95%) as colourless oily liquid.

**IR (neat) v<sub>max</sub>:** 3046, 2949, 1598, 1585, 965, 924, 882, 798 cm<sup>-1</sup>.

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):** δ 7.69-7.66 (m, 3H), 7.40 (d, J = 2.5 Hz, 1H), 7.35 (td, J = 8.0, 1 Hz, 1H), 7.26 (td, J = 7.0, 1 Hz, 1H), 7.20 (dd, J = 9.0, 2.5 Hz, 1H), 5.47 (t, J = 3.0 Hz, 1H), 3.89-3.84 (m, 1H), 3.56-3.53 (m, 1H), 1.98-1.93 (m, 1H), 1.84-1.79 (m, 2H), 1.63-1.54 (m, 2H), 1.52-1.47 (m, 1H) ppm.

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):** δ 155.1, 134.8, 129.7, 129.5, 127.9, 127.3, 126.5, 124.1, 119.4, 110.7, 96.6, 62.1, 30.6, 25.5, 19.0 ppm.

**MS:** m/z = 229 [M]<sup>+</sup>.



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