

Microwave-assisted allylation of acetals with allyltrimethylsilane in the presence of CuBr

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Supporting Information

General Information:

All reactions were carried out using a CEM Corporation Focused Microwave System, Model Discover. 1,2-Dichloroethane was dried over phosphorus pentoxide and distilled. All commercial reagents were used directly. NMR data was obtained on a 500 MHz spectrometer and IR data on an FT-IR spectrometer.

Representative Procedure:

In a typical experiment, 1.5 mmol CuBr was placed in a 10 ml glass pressure vial equipped with a stir bar. The pressure vial was closed using a PTFE-silicon septum (vial and septum available from CEM Corporation). Anhydrous 1,2-dichloroethane was added into the vial, followed by 1.5 mmol of the acetal **1** and 2.25 mmol of allyltrimethylsilane **2**. The suspension was heated with stirring at 100 °C for 60 min in the CEM microwave reactor described above. For the acetals **1f-1h**, 1.5 mmol of the acetal, 2.2 mmol CuBr, and 3 mmol of the silane **2** were used. After the completion of the reaction, the suspension was filtered, the volatiles removed in vacuo and the crude oils purified by flash chromatography. The isolated yields of the homoallyl ethers **3** are given in Table 1. We have not carried out the reaction on any scale larger than the 1.5 mmol described above due to the size limitations of the commercial microwave equipment we are using although we would expect that with a larger instrument, one could carry out the reaction on much larger scale.

4-Methoxy-4-phenyl-1-butene (**3a**)

¹H-NMR (500 MHz, CDCl₃): δ 7.4-7.3 (m, 5H, Ar), 5.8 (m, 1H), 5.1 (m, 2H), 4.2 (t, 1H,

$J = 5.9$ Hz), 3.3 (s, 3H), 2.6 (m, 1H), 2.5 (m, 1H). ^{13}C -NMR (126 MHz, CDCl_3): δ 141.7, 134.8, 128.3, 127.6, 126.7, 116.9, 83.6, 56.6, 42.5. IR (neat): ν 3028, 2980, 2936, 2821, 1641, 1454, 1357, 1100, 915, 700 cm^{-1} .

4-(4-Chlorophenyl)-4-methoxy-1-butene (3b)

^1H -NMR (500 MHz, CDCl_3): δ 7.3 (d, 2H, $J = 8.4$ Hz), 7.2 (d, 2H $J = 8.3$ Hz), 5.7 (m, 1H), 5.0 (m, 2H), 4.1 (t, 1H, $J = 6.7$ Hz), 3.2 (s, 3H), 2.5 (m, 1H), 2.3 (m, 1H). ^{13}C -NMR (126 MHz, CDCl_3): δ 140.0, 134.2, 133.1, 128.4, 128.2, 117.1, 82.8, 56.6, 42.3. IR (neat): ν 2982, 2934, 2823, 1598, 1598, 1489, 1090, 1015 cm^{-1} .

4-(4-Bromophenyl)-4-methoxy-1-butene (3c)

^1H -NMR (500 MHz, CDCl_3): δ 7.4 (d, 2H, $J = 8.3$ Hz), 7.1 (d, 2H $J = 8.3$ Hz), 5.7 (m, 1H), 5.0 (m, 2H), 4.1 (t, 1H, $J = 6.5$ Hz), 3.2 (s, 3H), 2.5 (m, 1H), 2.3 (m, 1H). ^{13}C -NMR (126 MHz, CDCl_3): δ 140.7, 134.2, 131.4, 128.4, 121.3, 117.3, 83.0, 56.7, 42.3. IR (neat): ν 3077, 2980, 2931, 2821, 1641, 1591, 1485, 1404, 1344, 1104, 1010, 917 cm^{-1} .

4-(3-Nitrophenyl)-4-methoxy-1-butene (3d)

^1H -NMR (500 MHz, CDCl_3): δ 8.2 (s, 1H), 8.1 (m, 1H), 7.6 (d, 1H, $J = 7.6$ Hz), 7.5 (m, 1H), 5.7 (m, 1H), 5.0 (m, 2H), 4.3 (t, 1H, $J = 6.6$ Hz), 3.2 (s, 3H), 2.5 (m, 1H), 2.4 (m, 1H). ^{13}C -NMR (126 MHz, CDCl_3): δ 148.4, 140.3, 133.4, 132.9, 129.3, 123.4, 122.0, 117.9, 82.7, 57.0, 42.2). IR (neat): ν 2932, 2830, 1530, 1349, 1108, 1058 cm^{-1} . EI-LRES: $m/z = 207$ [M^+] (100%).

4-(4-Propylphenyl)-4-ethoxy-1-butene (3e)

^1H -NMR (500 MHz, CDCl_3): δ 7.2 (d, 2H, $J = 8.0$ Hz), 7.1 (d, 2H, $J = 8.0$ Hz), 5.8 (m, 1H), 5.0 (m, 2H), 4.2 (t, 1H, $J = 6.1$ Hz), 3.4 (m, 2H), 2.6 (t, 3H, $J = 4.4$ Hz), 2.4 (m, 1H), 1.6 (m, 1H), 1.2 (t, 3H, $J = 7.0$ Hz), 1.0 (t, 3H, $J = 7.4$ Hz). ^{13}C -NMR (126 MHz, CDCl_3): δ 141.8, 139.5, 135.0, 128.4, 126.4, 116.4, 81.5, 63.9, 42.3, 37.6, 24.4, 15.2, 13.8. IR (neat): ν 2962, 2931, 2870, 1720, 1092, 917, cm^{-1} . EI-HRES: calc: 204.1470, found: 204.1461.

4-Methoxy-1-undecene (3f)

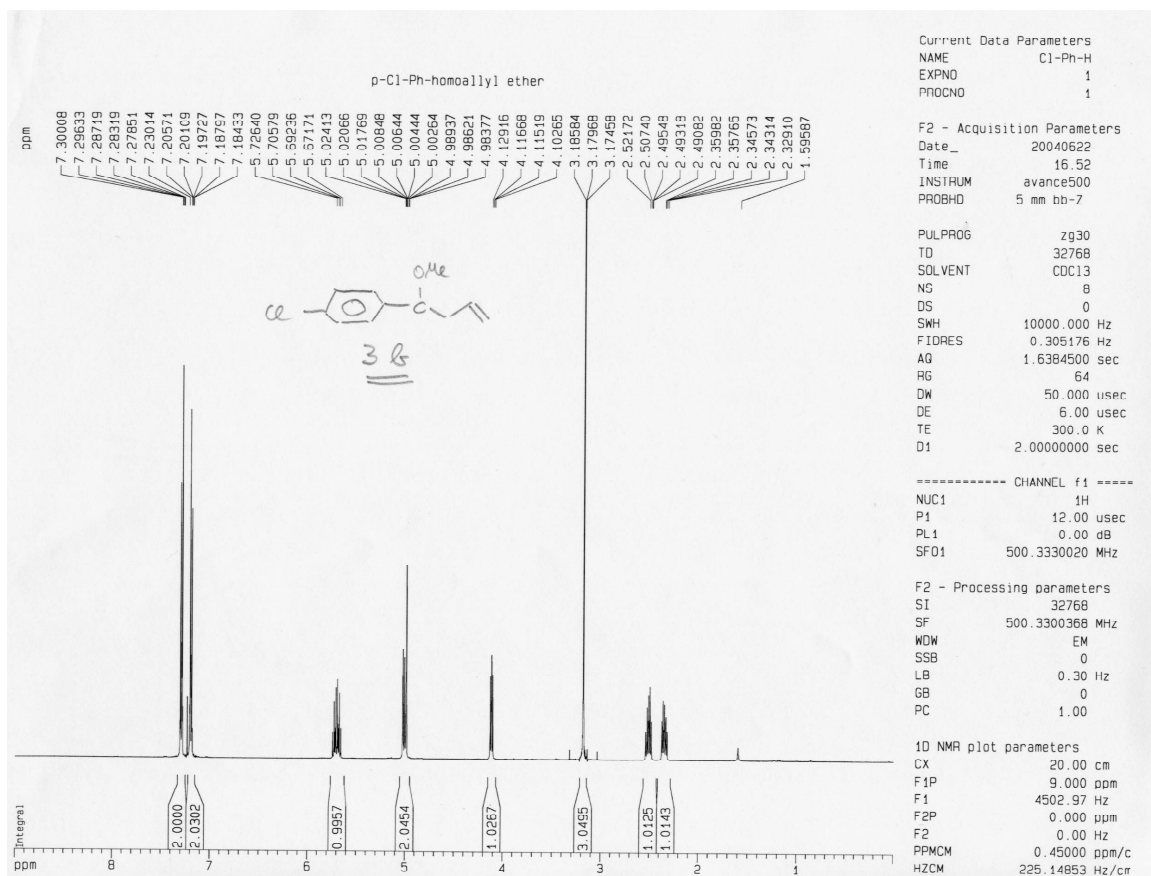
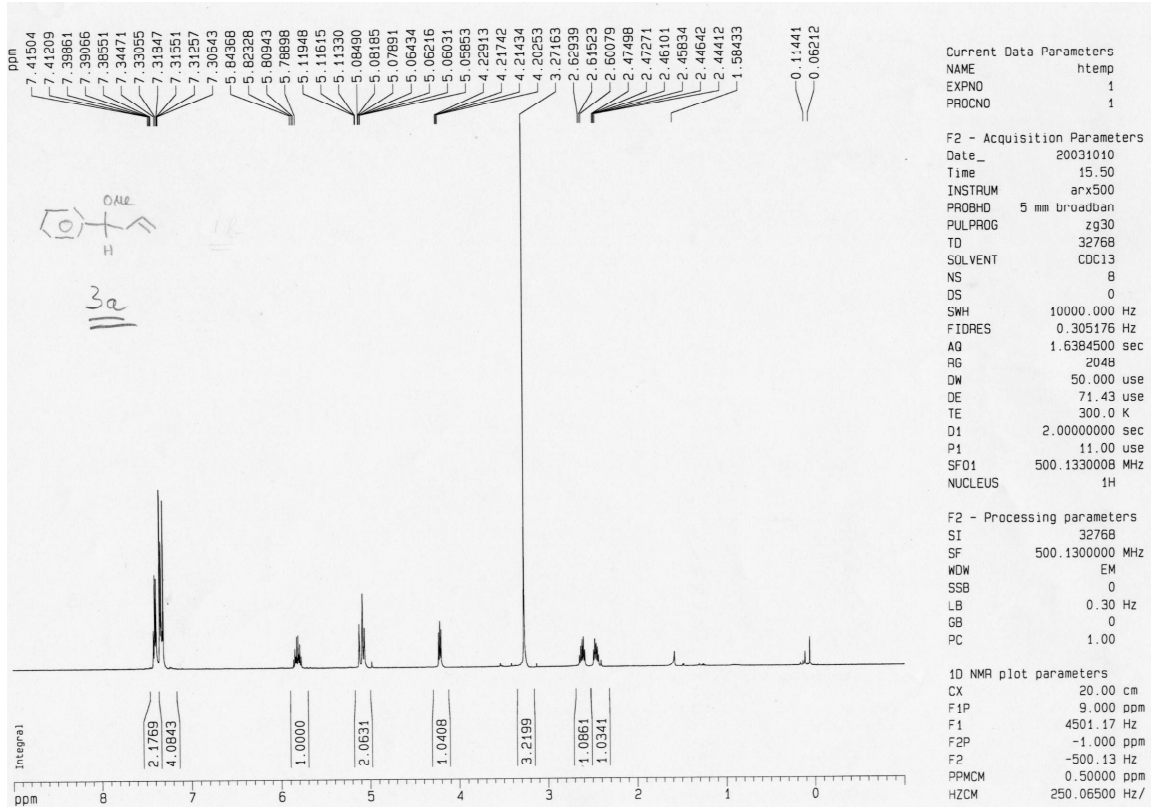
^1H -NMR (500 MHz, CDCl_3): δ 5.8 (m, 1H), 5.0 (m, 2H), 3.3 (s, 3H), 3.2 (m, 1H), 2.2 (m, 2H), 1.4-1.2 (m, 12H), 0.8 (m, 3H, $J = 6.2$ Hz). ^{13}C -NMR (126 MHz, CDCl_3): δ 135.0, 116.7, 80.5, 56.5, 37.8, 33.4, 31.8, 29.7, 29.3, 25.3, 22.7, 14.1. IR (neat): ν 2955, 2927, 2856, 1462, 1098, 911 cm^{-1} .

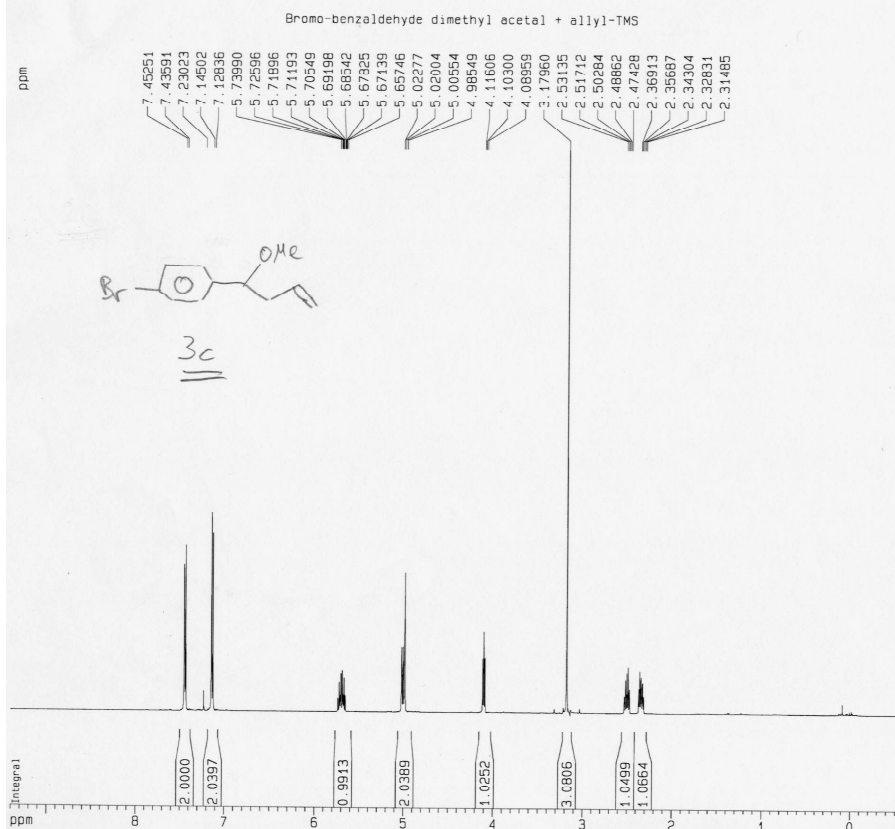
4-Methoxy-5-phenyl-1-pentene (3g)

^1H -NMR (500 MHz, CDCl_3): δ 7.3-7.2 (m, 5H), 5.8 (m, 1H), 5.1 (m, 2H), 3.4 (m, 1H), 3.3 (s, 3H), 2.8 (m, 1H), 2.7 (m, 1H), 2.2 (m, 2H). ^{13}C -NMR (126 MHz, CDCl_3): δ 138.9, 134.7, 129.4, 128.2, 126.1, 117.1, 81.7, 57.0, 39.8, 37.5. IR (neat): ν 3027, 2928, 2823, 1641, 1495, 1454, 1359, 1098, 914, 745, 700 cm^{-1} .

1-Methoxy-1-(2-propenyl)-cyclohexane (3h)

^1H -NMR (500 MHz, CDCl_3): δ 5.8 (m, 1H), 5.0 (m, 2H), 3.1 (s, 3H), 2.2 (d, 2H, $J = 7.2$ Hz), 1.6-1.2 (m, 10H). ^{13}C -NMR (126 MHz, CDCl_3): δ 134.0, 117.1, 74.8, 48.1, 40.9, 33.8, 25.8, 21.8. IR (neat): ν 2931, 2855, 2823, 1639, 1455, 1081, 910 cm^{-1} .





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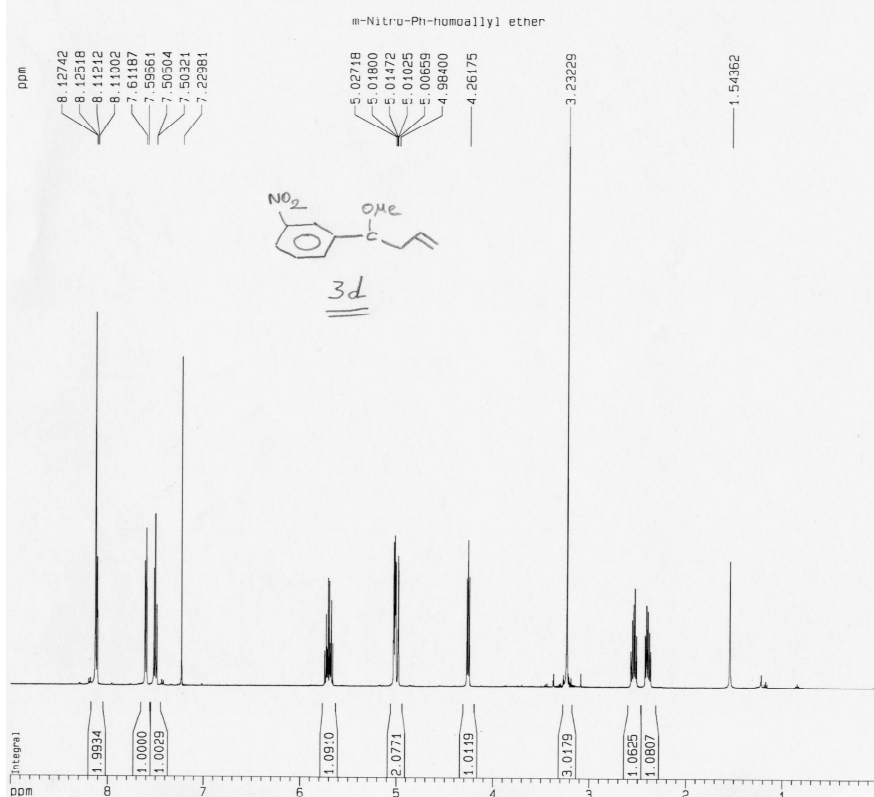
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