

Supporting Information for:

Regioselective Heck Arylation of Unsaturated Alcohols by

Palladium Catalysis in Ionic Liquid

Jun Mo, Lijin Xu, Jiwu Ruan, Shifang Liu and Jianliang Xiao*

Liverpool Centre for Materials and Catalysis

Department of Chemistry, University of Liverpool, Liverpool L69 7ZD, UK

E-mail: j.xiao@liv.ac.uk

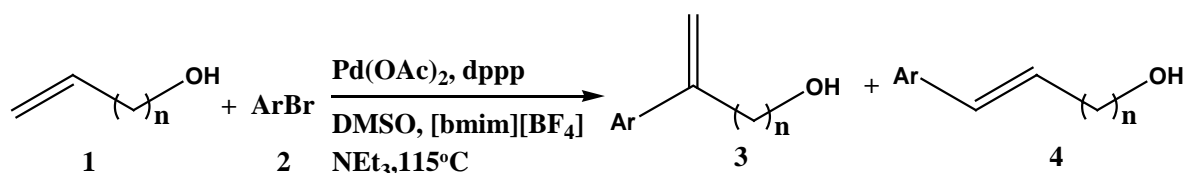
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A. Materials

All reactions were carried out under a nitrogen atmosphere. Chromatographic purifications were performed on silica gel (mesh 230-400) by the flash technique. 1-Butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]) was prepared according to the literature method.¹ Following vacuum-drying at 80 °C for 8 h, the ionic liquid was stored under nitrogen at ambient temperature and ready to use. AgNO₃ titration showed the chloride content of the ionic liquid to be below detection limit (<0.2%). Unsaturated alcohols **1a-f**, aryl halides **2a-p**, Pd(OAc)₂, 1,3-bis(diphenylphosphino)propane (DPPP) and triethylamine were purchased from Lancaster, Aldrich and TCI and were used as received. ¹H and ¹³C NMR spectra were recorded on a Gemini 400 spectrometer at 400

(^1H) and 100 MHz (^{13}C) in ppm with reference to TMS internal standard in CDCl_3 . Mass spectra were obtained by chemical ionization (CI). All the products were satisfactorily characterized by ^1H and ^{13}C NMR, MS, and HRMS, element analysis and when possible, comparison of their ^1H NMR spectra has been made with available literature data and/or those of authentic samples. The following compounds, 4-(1-hydroxymethyl-vinyl)-benzoic acid methyl ester (**3ad**),² 2-(4-fluorophenyl)-2-propen-1-ol (**3ae**),³ 2-phenyl-allyl alcohol (**3af**) [6006-81-1],⁴ 2-(4-methylphenyl)allyl alcohol (**3ag**) [66520-90-9],⁵ 3-p-fluorophenyl-3-buten-1-ol (**3be**) [29123-91-9],⁶ 4-hydroxy-2-phenyl-butene-(1) (**3bf**) [3174-83-2],⁷ 3-p-methylphenyl-3-buten-1-ol (**3bg**) [29128-22-1],⁸ 3-p-methoxyphenyl-3-buten-1-ol (**3bh**),⁹ 3-m-fluorophenyl-3-buten-1-ol (**3bj**),¹⁰ 3-m-methoxyphenyl-3-buten-1-ol (**3bk**) [29123-95-3],⁶ 3-(1-naphthyl)-3-buten-1-ol (**3bn**) [141171-90-6],⁷ and 4-(2-naphthyl)-4-penten-1-ol (**3co**) [127047-26-1],⁸ have all been reported previously.



B. General procedure for the Heck arylation

An oven-dried, two-necked round-bottom flask containing a stir bar was charged with an aryl halide **2** (1.0 mmol), $\text{Pd}(\text{OAc})_2$ (0.01-0.04 mmol), DPPP (0.02-0.08 mmol), DMSO (1 mL), and $[\text{bmim}][\text{BF}_4]$ (1 mL) under nitrogen at room temperature. Following degassing three times, unsaturated alcohol **1** [1.0 (**1d-1f**), or 2.0 (**1a-1c**) mmol] and NEt_3 (1.5 mmol) were injected sequentially. The flask was placed in an oil bath, and the mixture was stirred and heated at the desired temperature. After an appropriate reaction

time, the flask was removed from the oil bath and cooled to room temperature, the product extracted with CH₂Cl₂ (3 x 20 mL). The combined organic layer was washed with water until neutrality, dried (MgSO₄), filtered, and concentrated *in vacuo*. A small sample was then taken for NMR analysis. The arylated alcohol **3** was isolated out of the crude product by flash chromatography on silica gel using a mixture of ethyl acetate and hexane (20:80 to 80:20) as eluant. The isolated yields of the product are given in Tables 2-3.

C. Compounds characterized

[4-(1-Hydroxypro-2-en-2-yl)](phenyl)methanone (3ab). ¹H NMR (400 MHz, CDCl₃) δ 7.82-7.80 (m, 4H), 7.60-7.56 (m, 3H), 7.51-7.47 (m, 2H), 5.62 (s, 1H), 5.49 (s, 1H), 4.61 (s, 2H), 1.61 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 196.6, 146.8, 143.0, 138.0, 137.2, 132.8, 130.0, 130.4, 128.7, 126.4, 115.2, 65.2; CI-MS *m/z* 239 [(M + H)⁺, 100], 223 (30); HRMS Calcd for C₁₆H₁₅O₂ (M + H)⁺: 239.1072. Found: 239.1076; Anal. Calcd for C₁₆H₁₄O₂: C, 80.65; H, 5.92. Found: C, 80.48; H, 5.88.

1-[4-(1-Hydroxyprop-2-en-2-yl)phenyl]ethanone (3ac). ¹H NMR (400 MHz, CDCl₃) δ 7.96-7.93 (m, 2H), 7.57-7.53 (m, 2H), 5.59 (s, 1H), 5.48 (s, 1H), 4.57 (s, 2H), 2.60 (s, 3H), 1.55 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 197.9, 146.9, 143.6, 136.9, 129.0, 126.6, 115.2, 65.3, 27.2; CI-MS *m/z* 177 [(M + H)⁺, 100]; HRMS Calcd for C₁₁H₁₃O₂ (M + H)⁺: 177.0916. Found: 177.0912; Anal. Calcd for C₁₁H₁₂O₂: C, 74.98; H, 6.86. Found: C, 74.76; H, 6.83.

4-(1-Hydroxymethyl-vinyl)-benzoic acid methyl ester (3ad). ¹H NMR (400 MHz, CDCl₃) δ 8.03-8.00 (m, 2H), 7.53-7.50 (m, 2H), 5.58 (s, 1H), 5.47 (s, 1H), 4.56 (s, 2H), 3.92 (s, 3H), 1.84 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 169.9, 146.4, 143.0, 129.8, 129.4, 126.0, 114.7, 64.8, 52.2; CI-MS *m/z* 210 {[M + (NH₄)⁺], 100}; HRMS

Calcd for $C_{11}H_{16}NO_3$ $[M + (NH_4)^+]$: 210.1130. Found: 210.1133; Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29. Found: C, 69.01; H, 6.26.

2-(4-Fluorophenyl)-2-propen-1-ol (3ae). 1H NMR (400 MHz, $CDCl_3$) δ 7.45-7.42 (m, 2H), 7.07-7.02 (m, 2H), 5.43 (s, 1H), 5.34 (s, 1H), 4.52 (s, 2H), 1.60 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0 (d, $J_{CF} = 240$ Hz), 146.6, 136.0 (d, $J_{CF} = 4$ Hz), 128.2 (d, $J_{CF} = 8$ Hz), 115.9 (d, $J_{CF} = 21$ Hz), 113.1, 65.5; CI-MS m/z 170 $\{[M + (NH_4)^+]$, 100 $\}$, 151 (55); HRMS Calcd for $C_9H_{13}NFO$ $[M + (NH_4)^+]$: 170.0981. Found: 170.0980; Anal. Calcd for C_9H_9FO : C, 71.04; H, 5.96. Found: C, 70.84; H, 6.01.

2-Phenyl-allyl alcohol (3af). 1H NMR (400 MHz, $CDCl_3$) δ 7.47-7.44 (m, 2H), 7.37-7.28 (m, 3H), 5.47 (s, 1H), 5.36 (s, 1H), 4.58 (s, 2H), 1.53 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 138.6, 128.6, 127.9, 126.1, 112.7, 65.1; CI-MS m/z 152 $\{[M + (NH_4)^+]$, 100 $\}$; HRMS Calcd for $C_9H_{14}NO$ $[M + (NH_4)^+]$: 152.1075. Found: 152.1077; Anal. Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.36; H, 7.54.

2-(4-Methylphenyl)allyl alcohol (3ag). 1H NMR (400 MHz, $CDCl_3$) δ 7.36-7.34 (m, 2H), 7.17-7.15 (m, 2H), 5.44 (s, 1H), 5.31 (s, 1H), 4.54 (s, 2H), 2.35 (s, 3H), 1.52 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 137.6, 134.4, 129.2, 126.0, 114.8, 65.2, 21.2; CI-MS m/z 166 $\{[M + (NH_4)^+]$, 60 $\}$, 149 (45), 133 (100); HRMS Calcd for $C_{10}H_{16}NO$ $[M + (NH_4)^+]$: 166.1232. Found: 166.1233; Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.76; H, 8.13.

3-(3-Hydroxyprop-1-en-2-yl)benzotrile (3ai). 1H NMR (400 MHz, $CDCl_3$) δ 7.76-7.75 (m, 1H), 7.74-7.69 (m, 1H), 7.60-7.57 (m, 1H), 7.48-7.44 (m, 1H), 5.54 (s, 1H), 5.47 (s, 1H), 4.54 (s, 2H), 1.67 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 139.9, 131.3, 130.5, 129.9, 129.3, 118.7, 115.2, 112.8, 64.8; CI-MS m/z 177 $\{[M + (NH_4)^+]$, 100 $\}$; HRMS Calcd for $C_{10}H_{13}N_2O$ $[M + (NH_4)^+]$: 177.1028. Found: 177.1026; Anal.

Calcd for C₁₀H₉NO: C, 75.45; H, 5.70. Found: C, 75.21; H, 5.76.

2-(3-Fluorophenyl)-2-propen-1-ol (3aj). ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.15 (m, 3H), 7.01-7.00 (m, 1H), 5.51 (s, 1H), 5.40 (s, 1H), 4.52 (s, 2H), 1.67 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 163.3 (d, *J*_{CF} = 245 Hz), 146.6, 141.2 (d, *J*_{CF} = 7 Hz), 130.3 (d, *J*_{CF} = 9 Hz), 122.1 (d, *J*_{CF} = 3 Hz), 115.2 (d, *J*_{CF} = 21 Hz), 114.2, 113.4 (d, *J*_{CF} = 22 Hz), 65.3; CI-MS *m/z* 170 {[M + (NH₄)⁺], 100}, 152 (80), 151(80); HRMS Calcd for C₉H₁₃NFO [M + (NH₄)⁺]: 170.0981. Found: 170.0980; Anal. Calcd for C₉H₉FO: C, 71.04; H, 5.96. Found: C, 71.44; H, 6.02.

2-(2-Fluorophenyl)-2-propen-1-ol (3al). ¹H NMR (400 MHz, CDCl₃) δ 7.38-7.21 (m, 2H), 7.21-7.11 (m, 2H), 5.42 (s, 1H), 5.38 (s, 1H), 4.53 (s, 2H), 1.69 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 163.2 (d, *J*_{CF} = 243 Hz), 142.6, 131.3 (d, *J*_{CF} = 7 Hz), 129.9 (d, *J*_{CF} = 7 Hz), 129.0 (d, *J*_{CF} = 3 Hz), 124.6 (d, *J*_{CF} = 21 Hz), 118.7, 116.3 (d, *J*_{CF} = 23 Hz), 65.5; CI-MS *m/z* 170 {[M + (NH₄)⁺], 100}, 152 (80), 151 (100); HRMS Calcd for C₉H₁₃NFO [M + (NH₄)⁺]: 170.0981. Found: 170.0982; Anal. Calcd for C₉H₉FO: C, 71.04; H, 5.96. Found: C, 71.24; H, 5.94.

3-(2-Naphthyl)-3-propen-1-ol (3ao). ¹H NMR (400 MHz, CDCl₃) δ 7.86-7.79 (m, 4H), 7.60-7.58 (m, 1H), 7.48-7.42 (m, 2H), 5.60 (s, 1H), 5.44 (s, 1H), 4.63 (s, 2H), 1.67 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 147.5, 136.1, 133.8, 133.5, 128.6, 128.5, 128.0, 126.7, 126.5, 125.2, 124.7, 113.6, 65.5; CI-MS *m/z* 202 {[M + (NH₄)⁺], 100}, 185 (70), 169 (30); HRMS Calcd for C₁₃H₁₆NO [M + (NH₄)⁺]: 202.1232. Found: 202.1237; Anal. Calcd for C₁₃H₁₂O: C, 84.75; H, 6.57. Found: C, 84.86; H, 6.53.

2-(2-Methoxynaphthalen-6-yl)prop-2-en-1-ol (3ap). ¹H NMR (400 MHz, CDCl₃) δ 7.82-7.81 (m, 1H), 7.74-7.71 (m, 2H), 7.60-7.58 (m, 1H), 7.16-7.12 (m, 2H), 5.59 (s, 1H), 5.41 (s, 1H), 4.66 (s, 2H), 3.92 (s, 3H), 1.62 (s, 1H); ¹³C NMR (100 MHz,

CDCl₃) δ 157.9, 147.0, 134.2, 133.4, 129.8, 128.8, 127.0, 124.8, 124.6, 119.1, 112.5, 105.6, 65.2, 55.3; CI-MS m/z 215 [(M + H)⁺, 100], 199 (40); HRMS Calcd for C₁₄H₁₅O₂ (M + H)⁺: 215.1072. Found: 215.1077; Anal. Calcd for C₁₄H₁₄O₂: C, 78.48; H, 6.59. Found: C, 78.34; H, 6.56.

4-(4-Hydroxybut-1-en-2-yl)benzotrile (3ba). ¹H NMR (400 MHz, CDCl₃) δ 7.64-7.61 (m, 2H), 7.53-7.50 (m, 2H), 5.50 (s, 1H), 5.32 (s, 1H), 3.72 (t, J = 6.5 Hz, 2H), 2.79 (t, J = 6.5 Hz, 2H), 1.52 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 145.7, 144.1, 132.6, 127.2, 119.1, 117.6, 111.7, 61.3, 38.5; CI-MS m/z 191 {[M + (NH₄)⁺], 100}; HRMS Calcd for C₁₁H₁₅N₂O [M + (NH₄)⁺]: 191.1184. Found: 191.1181; Anal. Calcd for C₁₁H₁₁NO: C, 76.28; H, 6.40; N, 8.09; Found: C, 76.05; H, 6.39; N, 8.06.

1-[4-(1-Hydroxybut-2-en-2-yl)phenyl]ethanone (3bc). ¹H NMR (400 MHz, CDCl₃) δ 7.95-7.93 (m, 2H), 7.51-7.49 (m, 2H), 5.51 (s, 1H), 5.28 (s, 1H), 3.75 (t, J = 6.5 Hz, 2H), 2.81 (t, J = 6.5 Hz, 2H), 2.60 (s, 3H), 1.58 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 197.9, 145.6, 144.5, 136.7, 128.9, 126.6, 116.8, 61.3, 38.7, 26.9; CI-MS m/z 191 [(M + H)⁺, 100]; HRMS Calcd for C₁₂H₁₅O₂ (M + H)⁺: 191.1072. Found: 191.1070; Anal. Calcd for C₁₂H₁₄O₂: C, 75.76; H, 7.42. Found: C, 75.57; H, 7.40.

Methyl 4-(4-hydroxybut-1-en-2-yl)benzote (3bd). ¹H NMR (400 MHz, CDCl₃) δ 8.03-7.99 (m, 2H), 7.49-7.46 (m, 2H), 5.49 (s, 1H), 5.26 (s, 1H), 3.91 (s, 3H), 3.74 (t, J = 6.5 Hz, 2H), 2.80 (t, J = 6.5 Hz, 2H), 1.66 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 167.2, 145.6, 144.6, 130.3, 129.9, 126.5, 116.6, 61.4, 52.5, 38.7; CI-MS m/z 207 [(M + H)⁺, 100]; HRMS Calcd for C₁₁H₁₅N₂O (M + H)⁺: 207.1021. Found: 207.1021; Anal. Calcd for C₁₂H₁₄O₃: C, 69.88; H, 6.84. Found: C, 70.19; H, 6.87.

3-(4-Fluorophenyl)-3-buten-1-ol (3be). ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.37 (m, 2H), 7.04-7.01 (m, 2H), 5.35 (s, 1H), 5.16 (s, 1H), 3.72 (t, J = 6.5 Hz, 2H), 2.77 (t, J

= 6.5 Hz, 2H), 1.45 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.0 (d, $J_{\text{CF}} = 245$ Hz), 144.3, 136.9 (d, $J_{\text{CF}} = 4$ Hz), 128.2 (d, $J_{\text{CF}} = 8$ Hz), 115.5 (d, $J_{\text{CF}} = 15$ Hz), 114.9, 61.4, 39.1; CI-MS m/z 167 [(M + H) $^+$, 100], 149 (45); HRMS Calcd for $\text{C}_{10}\text{H}_{12}\text{FO}$ (M + H) $^+$: 167.0872. Found: 167.0870; Anal. Calcd for $\text{C}_{10}\text{H}_{11}\text{FO}$: C, 72.27; H, 6.67; Found: C, 72.02; H, 6.65.

4-Hydroxy-2-phenyl-1-butene (3bf). ^1H NMR (400 MHz, CDCl_3) δ 7.42-7.40 (m, 2H), 7.33-7.28 (m, 3H), 5.41 (s, 1H), 5.16 (s, 1H), 3.72 (t, $J = 6.5$ Hz, 2H), 2.79 (t, $J = 6.5$ Hz, 2H), 1.50 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.3, 140.9, 129.1, 128.6, 126.5, 114.9, 61.4, 39.0; CI-MS m/z 163 [(M + H) $^+$, 95], 145 (45), 133 (100); HRMS Calcd for $\text{C}_{11}\text{H}_{15}\text{O}$ (M + H) $^+$: 163.1123. Found: 163.1118; Anal. Calcd for $\text{C}_{10}\text{H}_{12}\text{O}$: C, 81.04; H, 8.16. Found: C, 80.71; H, 8.12.

3-(4-Methylphenyl)-3-buten-1-ol (3bg). ^1H NMR (400 MHz, CDCl_3) δ 7.33-7.30 (m, 2H), 7.15-7.12 (m, 2H), 5.38 (s, 1H), 5.11 (s, 1H), 3.72 (t, $J = 6.4$ Hz, 2H), 2.77 (t, $J = 6.4$ Hz, 2H), 2.34 (s, 3H), 1.47 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.0, 137.9, 137.8, 129.6, 126.4, 114.1, 62.5, 39.0, 21.4; CI-MS m/z 149 [(M + H) $^+$, 100], 131 (55); HRMS Calcd for $\text{C}_{10}\text{H}_{13}\text{O}$ (M + H) $^+$: 149.0967. Found: 149.0970; Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{O}$: C, 81.44; H, 8.70. Found: C, 81.11; H, 8.65.

3-(4-Methoxyphenyl)-3-buten-1-ol (3bh). ^1H NMR (400 MHz, CDCl_3) δ 7.36-7.34 (m, 2H), 6.87-6.85 (m, 2H), 5.33 (s, 1H), 5.06 (s, 1H), 3.79 (s, 3H), 3.70 (t, $J = 6.5$ Hz, 2H), 2.74 (t, $J = 6.5$ Hz, 2H), 1.47 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.7, 144.5, 132.5, 127.9, 114.1, 113.9, 61.4, 55.7, 39.0; CI-MS m/z 179 [(M + H) $^+$, 26], 161 (40), 149 (100); HRMS Calcd for $\text{C}_{11}\text{H}_{15}\text{O}_2$ (M + H) $^+$: 179.1072. Found: 179.1075; Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{O}_2$: C, 74.13; H, 7.92. Found: C, 74.42; H, 7.95.

3-(4-Hydroxybut-1-en-2-yl)benzotrile (3bi). ^1H NMR (400 MHz, CDCl_3) δ

7.70-7.69 (m, 1H), 7.65-7.63 (m, 1H), 7.57-7.55 (m, 1H), 7.46-7.44 (m, 1H), 5.45 (s, 1H), 5.28 (s, 1H), 3.74 (t, $J = 6.5$ Hz, 2H), 2.52 (t, $J = 6.5$ Hz, 2H), 1.62 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.6, 142.4, 131.4, 130.8, 130.2, 129.7, 119.1, 116.9, 113.1, 61.2, 38.5; CI-MS m/z 191 $\{[\text{M} + (\text{NH}_4)^+], 100\}$; HRMS Calcd for $\text{C}_{11}\text{H}_{15}\text{N}_2\text{O}$ $[\text{M} + (\text{NH}_4)^+]$: 191.1184. Found: 191.1183; Anal. Calcd for $\text{C}_{11}\text{H}_{11}\text{NO}$: C, 76.28; H, 6.40; N, 8.09; Found: C, 76.35; H, 6.44; N, 8.07.

3-(3-Fluorophenyl)-3-buten-1-ol (3bj). ^1H NMR (400 MHz, CDCl_3) δ 7.23-7.17 (m, 1H), 7.12-7.06 (m, 1H), 7.00-6.95 (m, 1H), 6.93-6.87 (m, 1H), 5.42 (s, 1H), 5.15 (s, 1H), 3.74 (t, $J = 6.5$ Hz, 2H), 2.78 (t, $J = 6.5$ Hz, 2H), 1.60 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.1 (d, $J_{\text{CF}} = 244$ Hz), 144.3, 143.3 (d, $J_{\text{CF}} = 7$ Hz), 130.1 (d, $J_{\text{CF}} = 8$ Hz), 122.2 (d, $J_{\text{CF}} = 4$ Hz), 115.8 (d, $J_{\text{CF}} = 21$ Hz), 114.5, 113.4 (d, $J_{\text{CF}} = 23$ Hz), 61.4, 38.8; CI-MS m/z 167 $[(\text{M} + \text{H})^+, 100]$, 149 (35); HRMS Calcd for $\text{C}_{10}\text{H}_{12}\text{FO}$ $(\text{M} + \text{H})^+$: 167.0872. Found: 167.0871; Anal. Calcd for $\text{C}_{10}\text{H}_{11}\text{FO}$: C, 72.27; H, 6.67; Found: C, 71.98; H, 6.64.

3-(3-Methoxyphenyl)-3-buten-1-ol (3bk). ^1H NMR (400 MHz, CDCl_3) δ 7.28-7.24 (m, 1H), 7.02-6.95 (m, 2H), 6.85-6.82 (m, 1H), 5.41 (s, 1H), 5.16 (s, 1H), 3.82 (s, 3H), 3.70 (t, $J = 6.5$ Hz, 2H), 2.79 (t, $J = 6.5$ Hz, 2H), 1.62 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.1, 145.2, 142.4, 130.9, 119.1, 115.2, 113.3, 112.1, 61.4, 55.7, 39.1; CI-MS m/z 179 $[(\text{M} + \text{H})^+, 100]$, 161 (40); HRMS Calcd for $\text{C}_{11}\text{H}_{15}\text{O}_2$ $(\text{M} + \text{H})^+$: 179.1072. Found: 179.1067; Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{O}_2$: C, 74.13; H, 7.92. Found: C, 73.90; H, 7.89.

3-(2-Fluorophenyl)-3-buten-1-ol (3bl). ^1H NMR (400 MHz, CDCl_3) δ 7.28-7.21 (m, 2H), 7.11-7.01 (m, 2H), 5.32 (s, 1H), 5.28 (s, 1H), 3.65 (t, $J = 6.4$ Hz, 2H), 2.74 (t, $J = 6.4$ Hz, 2H), 1.71 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.2 (d, $J_{\text{CF}} = 246$ Hz), 141.8, 130.3, 129.9, 129.5, 124.5, 118.5, 116.1 (d, $J_{\text{CF}} = 23$ Hz), 61.1, 40.1; CI-MS m/z

167 [(M + H)⁺, 100], 149 (30); HRMS Calcd for C₁₀H₁₂FO (M + H)⁺: 167.0872. Found: 167.0871; Anal. Calcd for C₁₀H₁₁FO: C, 72.27; H, 6.67; Found: C, 72.34; H, 6.69.

3-(2-Methoxyphenyl)-3-buten-1-ol (3bm). ¹H NMR (400 MHz, CDCl₃) δ 7.27-7.23 (m, 1H), 7.14-7.11 (m, 1H), 6.94-6.87 (m, 2H), 5.26 (s, 1H), 5.11 (s, 1H), 3.81 (s, 3H), 3.58 (t, *J* = 6.3 Hz, 2H), 2.71 (t, *J* = 6.3 Hz, 2H), 1.91 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 156.8, 145.1, 131.7, 130.3, 127.8, 121.4, 117.5, 111.1, 61.0, 55.9, 40.7; CI-MS *m/z* 179 [(M + H)⁺, 100], 161 (65), 149 (30); HRMS Calcd for C₁₁H₁₅O₂ (M + H)⁺: 179.1072. Found: 179.1068; Anal. Calcd for C₁₁H₁₄O₂: C, 74.13; H, 7.92. Found: C, 74.36; H, 7.88.

3-(1-Naphthyl)-3-buten-1-ol (3bn). ¹H NMR (400 MHz, CDCl₃) δ 8.01-8.00 (m, 1H), 7.84-7.82 (m, 1H), 7.78-7.74 (m, 1H), 7.48-7.40 (m, 3H), 7.29-7.25 (m, 1H), 5.49 (s, 1H), 5.21 (s, 1H), 3.64 (t, *J* = 6.4 Hz, 2H), 2.78 (t, *J* = 6.4 Hz, 2H), 1.50 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 145.9, 140.8, 134.2, 131.5, 128.8, 127.9, 126.4, 126.2, 125.9, 125.6, 125.5, 118.1, 61.1, 42.0; CI-MS *m/z* 199 [(M + H)⁺, 100], 181 (35), 169 (45); HRMS Calcd for C₁₄H₁₅O (M + H)⁺: 199.1123. Found: 199.1124; Anal. Calcd for C₁₄H₁₄O: C, 84.81; H, 7.12. Found: C, 84.57; H, 7.15.

3-(2-Naphthyl)-3-buten-1-ol (3bo). ¹H NMR (400 MHz, CDCl₃) δ 7.82-7.77 (m, 4H), 7.57-7.54 (m, 1H), 7.48-7.41 (m, 2H), 5.53 (s, 1H), 5.24 (s, 1H), 3.75 (t, *J* = 6.5 Hz, 2H), 2.87 (t, *J* = 6.5 Hz, 2H), 1.65 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 145.1, 138.1, 133.8, 133.4, 128.6, 127.7, 127.5, 126.8, 126.7, 125.3, 124.9, 115.4, 61.6, 39.0; CI-MS *m/z* 199 [(M + H)⁺, 100]; HRMS Calcd for C₁₄H₁₅O (M + H)⁺: 199.1123. Found: 199.1128; Anal. Calcd for C₁₄H₁₄O: C, 84.81; H, 7.12. Found: C, 84.47; H, 7.14.

Methyl 4-[(*E*)-4-hydroxybut-1-enyl]benzote (4bd). ¹H NMR (400 MHz, CDCl₃) δ 7.99-7.96 (m, 2H), 7.42-7.40 (m, 2H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.35 (dt, *J* = 16.0, 6.9

Hz, 1H), 3.91 (s, 3H), 3.79 (t, $J = 6.3$ Hz, 2H), 2.51 (dt, $J = 6.3, 6.9$ Hz, 2H), 1.51 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.3, 142.2, 132.2, 130.3, 129.9, 129.1, 126.3, 62.3, 52.4, 36.8; CI-MS m/z 207 $[(\text{M} + \text{H})^+, 100]$; HRMS Calcd for $\text{C}_{11}\text{H}_{15}\text{N}_2\text{O}$ $(\text{M} + \text{H})^+$: 207.1021. Found: 207.1023; Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{O}_3$: C, 69.88; H, 6.84. Found: C, 70.12; H, 6.81.

1-[4-(5-Hydroxypent-1-en-2-yl)phenyl]ethanone (3cc). ^1H NMR (400 MHz, CDCl_3) δ 7.93-7.90 (m, 2H), 7.51-7.48 (m, 2H), 5.40 (s, 1H), 5.21 (s, 1H), 3.67 (t, $J = 6.4$ Hz, 2H), 2.63 (t, $J = 6.5$ Hz, 2H), 2.60 (s, 3H), 1.75-1.71 (m, 2H), 1.58 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.1, 147.6, 146.3, 136.5, 129.0, 126.8, 114.9, 62.6, 31.8, 31.5, 26.9; CI-MS m/z 205 $[(\text{M} + \text{H})^+, 100]$; HRMS Calcd for $\text{C}_{13}\text{H}_{17}\text{O}_2$ $(\text{M} + \text{H})^+$: 205.1229. Found: 205.1232; Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{O}_2$: C, 76.44; H, 7.90. Found: C, 76.52; H, 7.94.

1-[4-(6-Hydroxyhex-1-en-2-yl)phenyl]ethanone (3dc). ^1H NMR (400 MHz, CDCl_3) δ 7.93-7.90 (m, 2H), 7.49-7.47 (m, 2H), 5.37 (s, 1H), 5.18 (s, 1H), 3.62 (t, $J = 6.3$ Hz, 2H), 2.57 (t, $J = 6.5$ Hz, 2H), 2.55 (s, 3H), 1.64-1.51 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.1, 147.9, 146.5, 136.4, 129.0, 126.7, 114.8, 63.0, 35.3, 32.7, 26.4, 24.8; CI-MS m/z 219 $[(\text{M} + \text{H})^+, 100]$; HRMS Calcd for $\text{C}_{14}\text{H}_{19}\text{O}_2$ $(\text{M} + \text{H})^+$: 219.1385. Found: 219.1389; Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_2$: C, 77.03; H, 8.31. Found: C, 76.69; H, 8.27.

1-[4-(7-Hydroxyhept-1-en-2-yl)phenyl]ethanone (3ec). ^1H NMR (400 MHz, CDCl_3) δ 7.93-7.89 (m, 2H), 7.49-7.46 (m, 2H), 5.36 (s, 1H), 5.17 (s, 1H), 3.64 (t, $J = 6.3$ Hz, 2H), 2.60 (s, 3H), 2.57 (t, $J = 6.4$ Hz, 2H), 1.60-1.50 (m, 7H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.7, 147.7, 146.2, 136.1, 128.6, 127.2, 114.3, 62.8, 39.0, 33.5, 28.7, 27.1, 25.8; CI-MS m/z 233 $[(\text{M} + \text{H})^+, 100]$; HRMS Calcd for $\text{C}_{15}\text{H}_{21}\text{O}_2$ $(\text{M} + \text{H})^+$: 233.1541. Found: 233.1544; Anal. Calcd for $\text{C}_{15}\text{H}_{20}\text{O}_2$: C, 77.55; H, 8.68. Found: C, 77.78; H, 8.82.

1-[4-(8-Hydroxyoct-1-en-2-yl)phenyl]ethanone (3fc). ^1H NMR (400 MHz,

CDCl₃) δ 7.93-7.90 (m, 2H), 7.49-7.46 (m, 2H), 5.37 (s, 1H), 5.18 (s, 1H), 3.63 (t, $J = 6.3$ Hz, 2H), 2.61 (s, 3H), 2.58 (t, $J = 6.3$ Hz, 2H), 1.60-1.49 (m, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 197.5, 147.2, 146.3, 136.5, 128.6, 127.1, 114.1, 62.9, 37.8, 33.2, 31.0, 29.0, 27.1, 25.8; CI-MS m/z 247 [(M + H)⁺, 100]; HRMS Calcd for C₁₆H₂₃O₂ (M + H)⁺: 247.1698. Found: 247.1699; Anal. Calcd for C₁₆H₂₂O₂: C, 78.01; H, 9.00. Found: C, 77.88; H, 9.02.

4-(2-Naphthyl)-4-penten-1-ol (3co). ¹H NMR (400 MHz, CDCl₃) δ 7.82-7.74 (m, 4H), 7.57-7.55 (m, 1H), 7.47-7.40 (m, 2H), 5.43 (s, 1H), 5.18 (s, 1H), 3.65 (t, $J = 6.5$ Hz, 2H), 2.70 (t, $J = 6.5$ Hz, 2H), 1.79-1.72 (m, 2H), 1.51 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 148.3, 138.5, 133.3, 132.7, 128.6, 128.5, 128.3, 127.0, 126.6, 125.1, 124.8, 113.5, 62.7, 32.9, 32.0; CI-MS m/z 213 [(M + H)⁺, 100]; HRMS Calcd for C₁₅H₁₇O (M + H)⁺: 213.1279. Found: 213.1278; Anal. Calcd for C₁₅H₁₆O: C, 84.87; H, 7.60. Found: C, 84.78; H, 7.66.

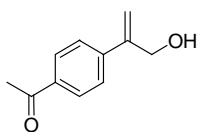
5-(2-Naphthyl)-5-hexen-1-ol (3do). ¹H NMR (400 MHz, CDCl₃) δ 7.83-7.76 (m, 4H), 7.59-7.54 (m, 1H), 7.47-7.39 (m, 2H), 5.41 (s, 1H), 5.15 (s, 1H), 3.62 (t, $J = 6.5$ Hz, 2H), 2.63 (t, $J = 6.4$ Hz, 2H), 1.64-1.57 (m, 4H), 1.42 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 148.6, 139.0, 133.3, 130.7, 128.9, 128.6, 128.0, 127.6, 126.4, 126.1, 125.1, 113.4, 63.2, 35.5, 33.0, 26.5; CI-MS m/z 227 [(M + H)⁺, 100]; HRMS Calcd for C₁₆H₁₉O (M + H)⁺: 227.1436. Found: 227.1437; Anal. Calcd for C₁₆H₁₈O: C, 84.91; H, 8.02. Found: C, 84.55; H, 7.96.

6-(2-Naphthyl)-6-hepten-1-ol (3eo). ¹H NMR (400 MHz, CDCl₃) δ 7.83-7.74 (m, 4H), 7.57-7.55 (m, 1H), 7.48-7.40 (m, 2H), 5.40 (s, 1H), 5.15 (s, 1H), 3.61 (t, $J = 6.5$ Hz, 2H), 2.62 (t, $J = 6.4$ Hz, 2H), 1.63-1.40 (m, 7H); ¹³C NMR (100 MHz, CDCl₃) δ 148.8, 139.0, 133.8, 133.2, 128.5, 128.2, 127.9, 127.7, 126.2, 125.6, 125.1, 113.2, 63.3,

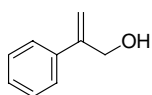
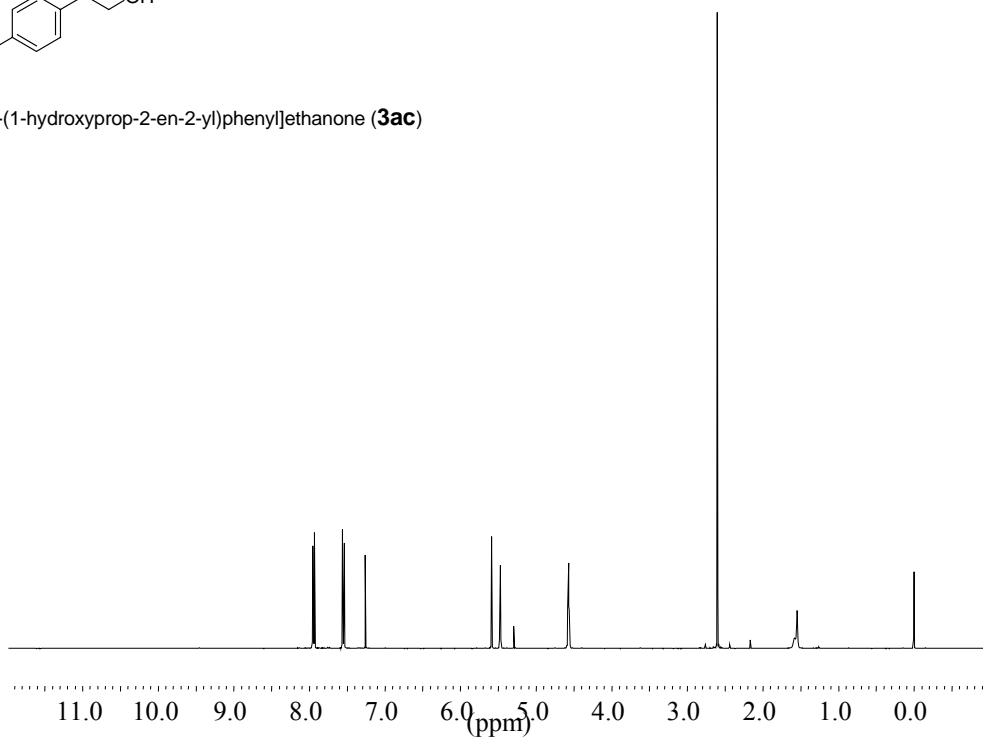
35.7, 33.0, 28.5, 25.9; CI-MS m/z 241 [(M + H)⁺, 100]; HRMS Calcd for C₁₇H₂₁O (M + H)⁺: 241.1592. Found: 241.1594; Anal. Calcd for C₁₇H₂₀O: C, 84.96; H, 8.39. Found: C, 85.04; H, 8.36.

7-(2-Naphthyl)-7-octen-1-ol (3fo). ¹H NMR (400 MHz, CDCl₃) δ 7.82-7.74 (m, 4H), 7.57-7.54 (m, 1H), 7.47-7.39 (m, 2H), 5.41 (s, 1H), 5.15 (s, 1H), 3.58 (t, J = 6.5 Hz, 2H), 2.61 (t, J = 6.4 Hz, 2H), 1.59-1.40 (m, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 148.9, 139.0, 133.8, 132.5, 128.7, 128.5, 128.3, 128.0, 127.8, 126.8, 125.6, 113.2, 63.4, 35.7, 33.0, 29.6, 29.0, 26.0; CI-MS m/z 255 [(M + H)⁺, 100]; HRMS Calcd for C₁₈H₂₃O (M + H)⁺: 255.1749. Found: 255.1750; Anal. Calcd for C₁₈H₂₂O: C, 84.99; H, 8.72. Found: C, 85.21; H, 8.68.

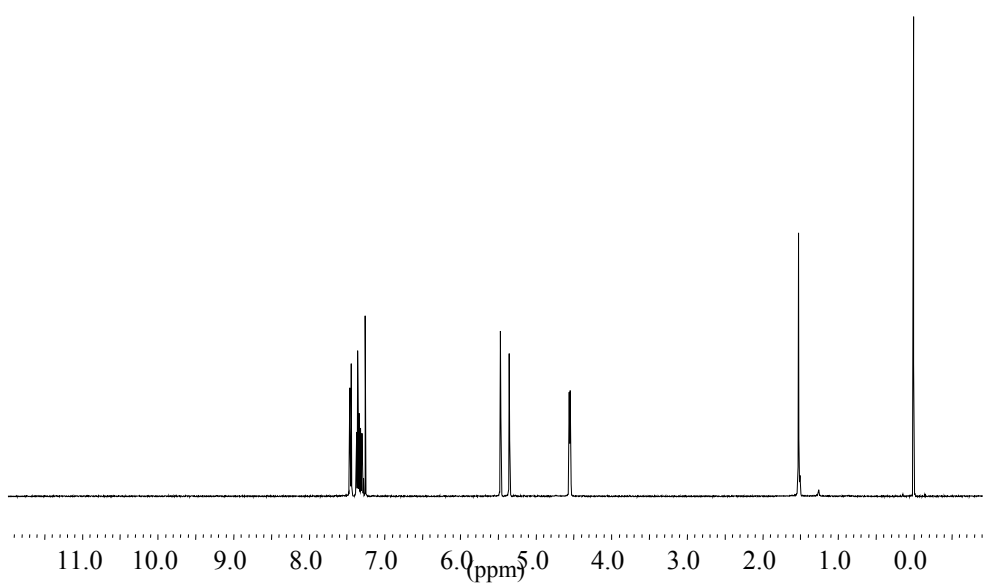
D. Sample ^1H NMR spectra

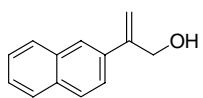


1-[4-(1-hydroxyprop-2-en-2-yl)phenyl]ethanone (**3ac**)

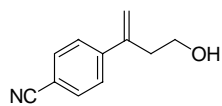
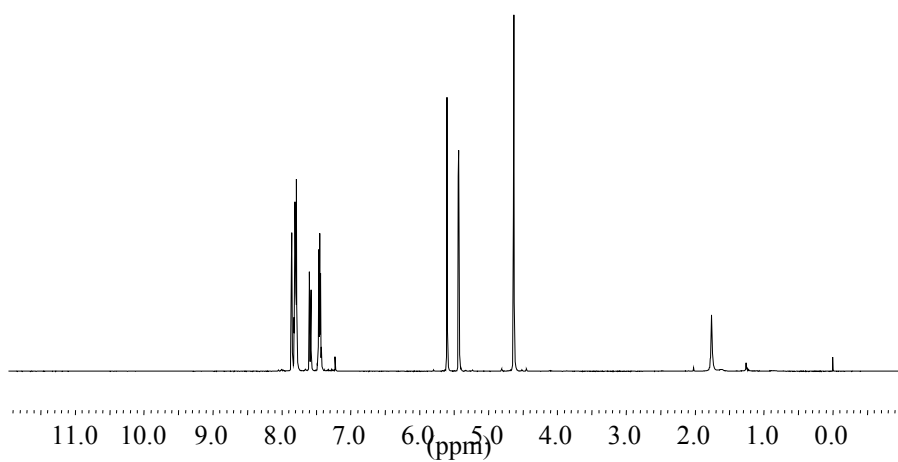


2-phenyl-allyl alcohol (**3af**)

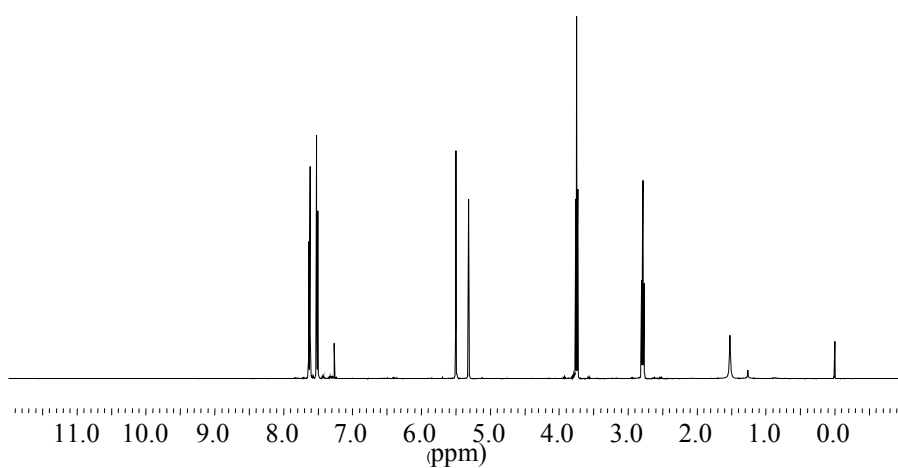


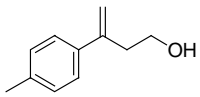


3-(2-naphthyl)-3-propen-1-ol (**3ao**)

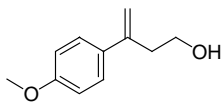
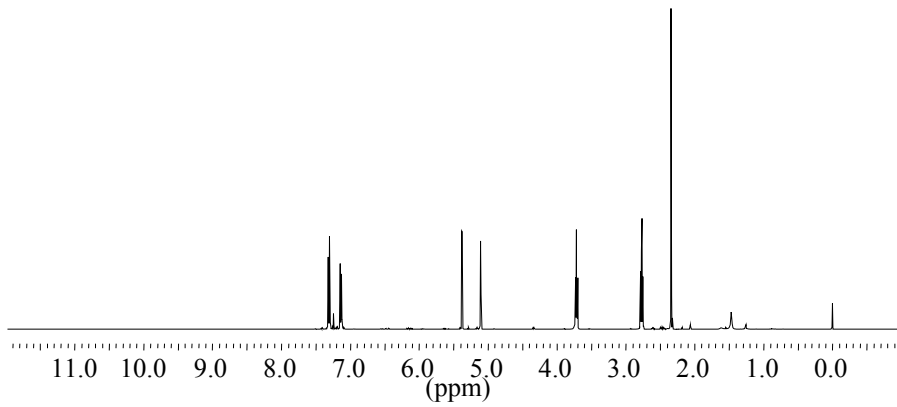


4-(4-hydroxybut-1-en-2-yl)benzonitrile (**3ba**)

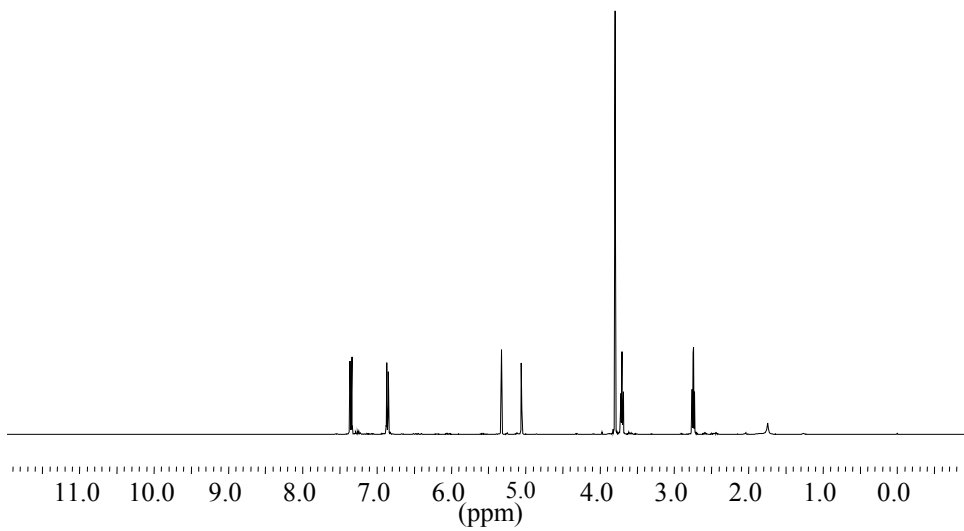


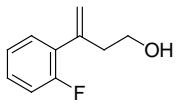


3-p-methylphenyl-3-buten-1-ol (**3bg**)

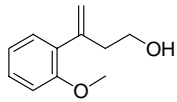
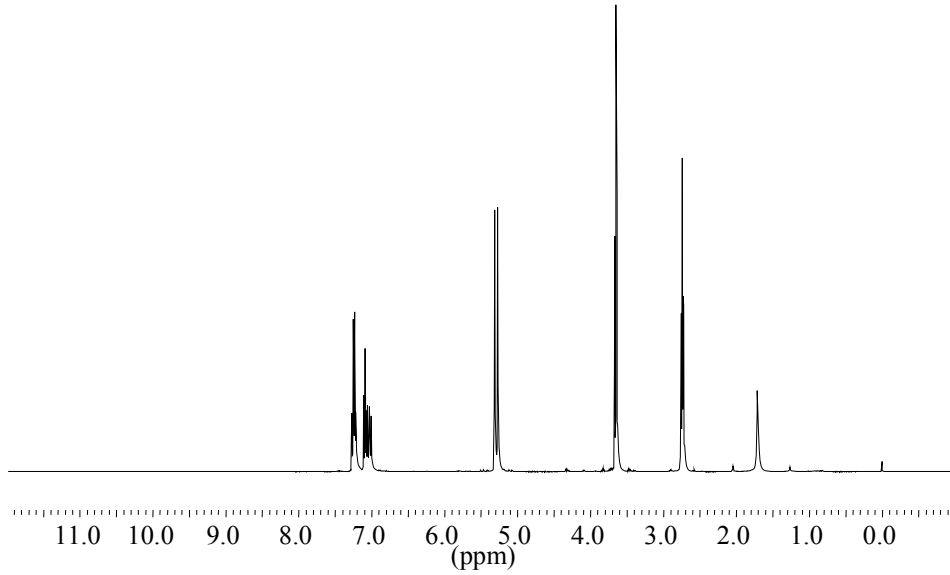


3-p-methoxyphenyl-3-buten-1-ol (**3bh**)

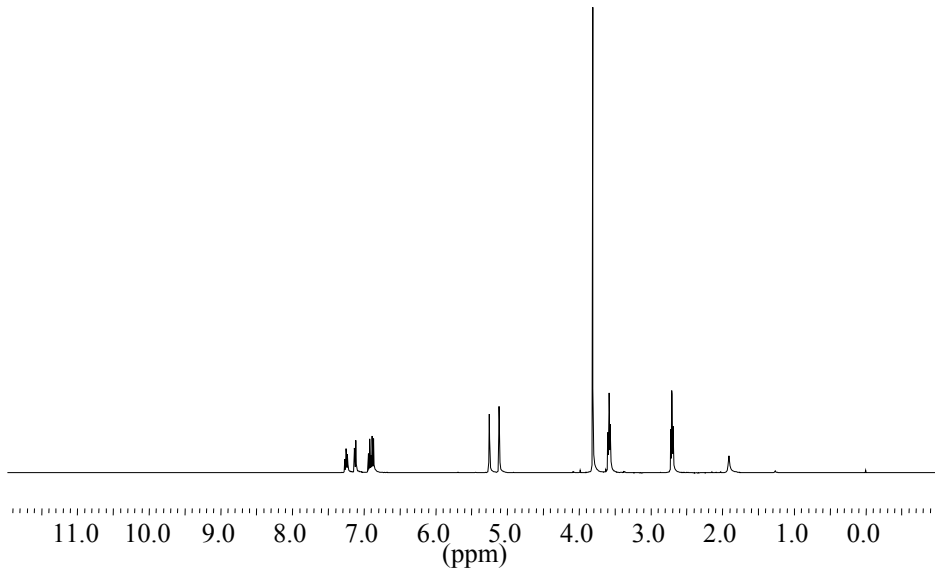


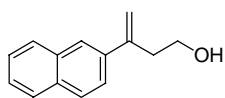


3-o-fluorophenyl-3-buten-1-ol (**3bl**)

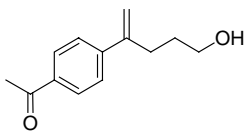
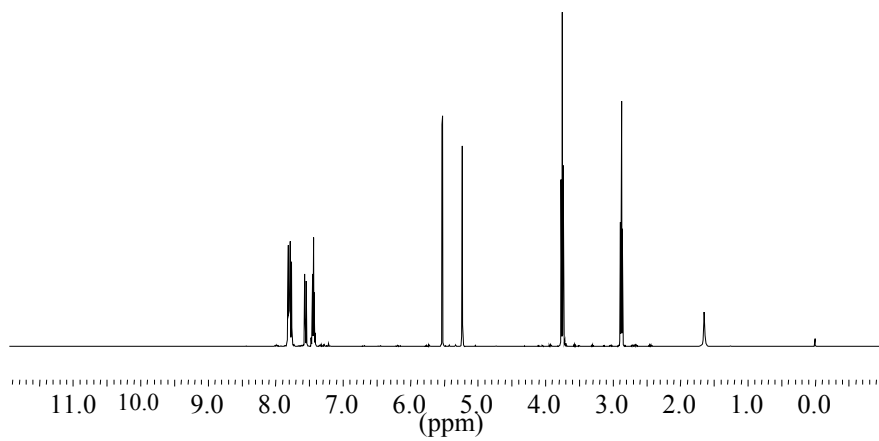


3-o-methoxyphenyl-3-buten-1-ol (**3bm**)

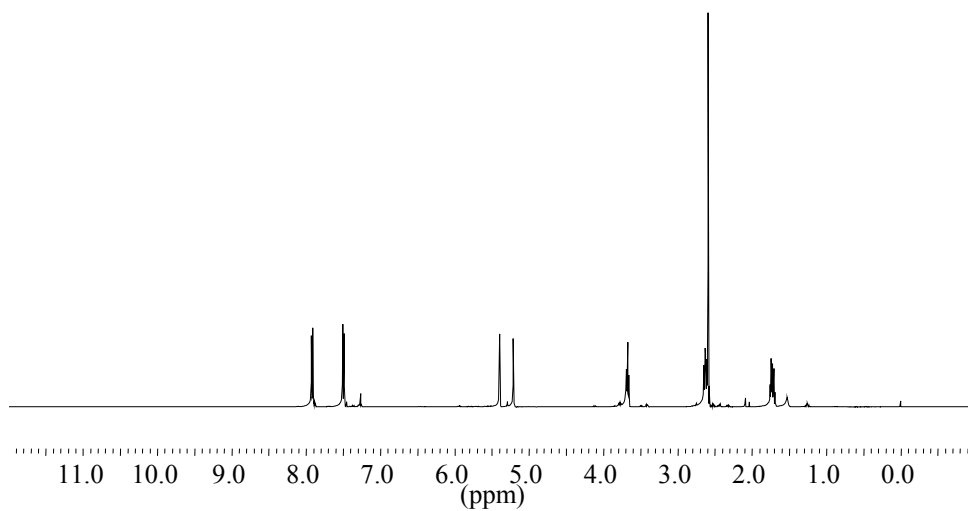


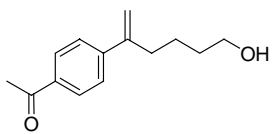


3-(2-naphthyl)-3-buten-1-ol (**3bo**)

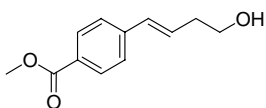
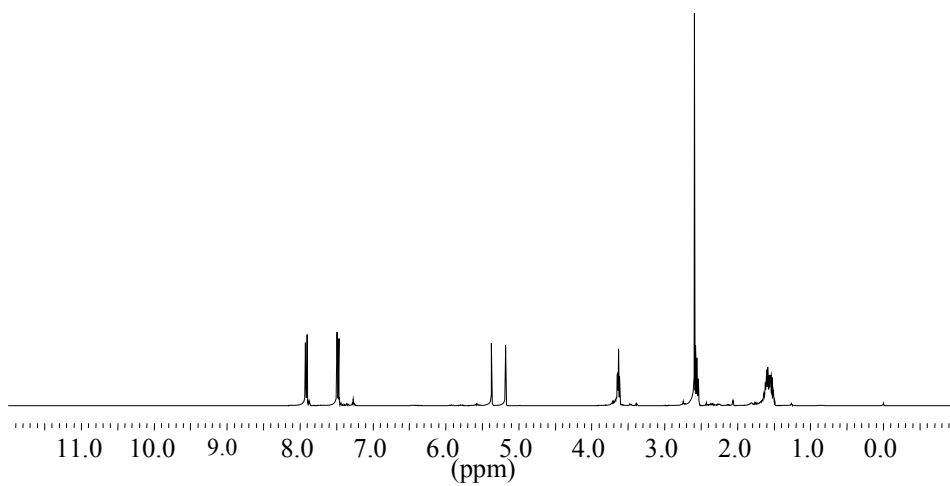


1-[4-(5-hydroxypent-1-en-2-yl)phenyl]ethanone (**3cc**)

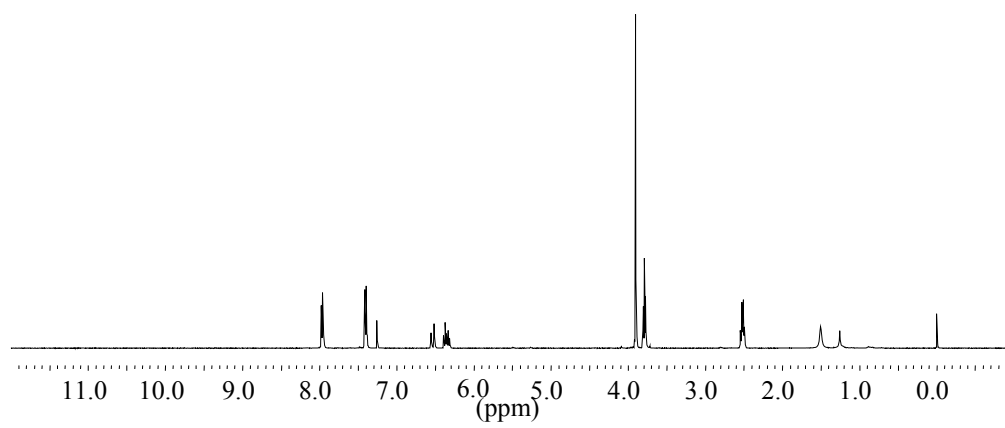




1-[4-(6-hydroxyhex-1-en-2-yl)phenyl]ethanone (**3dc**)



Methyl 4-[(E)-4-hydroxybut-1-enyl]benzoate (**4bd**)



E. References

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