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Supporting Information for:

Low Temperature Deoxygenations Through C-O Activation of Non-Activated Alcohols via Halide Catalysis

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General Procedures

All reagents and solvents were used as received unless noted otherwise. Stirbars used in catalytic reactions were cleaned with aqua regia for at least 3 h under gentle stirring, rinsed with copious amounts of water, and dried in an oven at 120 °C prior to use. All liquid reagents were dispensed by difference using gas-tight Hamilton syringes. Yields are reported as average yields of at least 2 experiments. The reported error is the standard deviation of at least two replicate trials.

GC analyses were performed on an Agilent 7890A Series GC equipped with FID detector, an Agilent HP-5 capillary column (length 30m, diameter 0.32 mm, film thickness 0.25 μm), and a 7693A auto injector module. Yields were calculated by calibrating prepared samples and standard to the response of the instrument. GC-MS investigations were carried out on an Agilent 5975C instrument using a 19091S-433 (HP-5MS; 30 m, 0.25 mm i.d., 0.25 μm df) column. The identities of all dehydration products were verified by comparison of the obtained data with GC and GC-MS data of original samples.

All reactions were conducted without rigorous exclusion of air and moisture unless noted otherwise. *para*-Xylene for dehydration reactions was obtained from MP Biomedicals and stored over activated 4 Å molecular sieves. All ionic liquids were stored in a glovebox at room temperature (N_2 atmosphere) prior to use. Acetamide, BiI_3, Celite, choline chloride, $CoBr_2$, $Cu(NO_3)_2$, CuCl, $CuBr_2$, CuI, $Cu(OTf)_2$, $FeSO_4$, $FeBr_2$, $FeCl_3$, glycerol, $NiCl_2$, NiI_2, $NiSO_4$, $Ni(NO_3)_2$, KNO_3, 1-octanol, 3-octanol, 2-phenylethanol, tetrabutylammonium bromide, tetra-*n*-butylammonium trifluromethanesulfonate, tetrahexylammonium iodide, tributylmethylammonium chloride, tetrahexylammonium bromide, urea, $ZnBr_2$, $ZnCl_2$, and $Zn(OTf)_2$ were purchased from Alfa Aesar. $Cu(OAc)_2$, dioctyl ether, $Fe(OTf)_3$, $Mn(OAc)_2$, tetrabutylammonium iodide, and 2-octanol were purchased from Sigma Aldrich. $Co(NO_3)_2$, $CuCl_2$, $BiBr_3$, $CuSO_4$, $Fe(NO_3)_3$, and $Ni(OTf)_2$ were purchased from Strem. $BiCl_3$, 1-bromooctane, 1,2-cyclohexanediol, 1-hexanol, 1-methylcyclopentanol, and 1-octene and were purchased from TCI. 1-butyl-3-methylimidazolium trifluromethanesulfonate and $NiBr_2$ were purchased from Acros.

General Procedure A: 1-Octanol Dehydration in Organic Solvents

Preactivated heteropolyacid (5.0 mol %) and metal co-catalyst (5.0 mol %) were added to a 4 mL scintillation vial equipped with a Teflon-coated stirbar under N_2 atmosphere (glovebox). After removing the vial from the glovebox, solvent (1.0 mL; dried over 4Å MS before use) and 1-octanol (0.100 ml, 82.7 mg, 0.635 mmol, 1.00 equiv) were added to the mixture.

The vial was sealed with a Teflon-lined cap and heated to 125 °C on a pre-heated vial plate under vigorous stirring (1500 rpm). After the reaction time was completed (Typically 48 h) the vial was taken off the heating block and the mixture was allowed to cool to room temperature. 10 µL PhOAc were added as GC-standard. The mixture was diluted with diethyl ether (3 mL) and extracted with 2 mL of saturated aqueous K_2CO_3 solution. The organic phase was filtered through celite and the filtrate was diluted to 10 mL with diethyl ether. The yield of products was determined by calibrated GC analysis.

Preactivation and Evaluation of Heteropolyacid Catalysts

Heteropolyacids were purchased either as solids ($H_3PW_{12}O_{40}$; $H_4SiW_{12}O_{40}$) or as solutions ($H_3PMo_{12}O_{40}$; 20% solution in EtOH from Sigma Aldrich). In order to isolate the respective $H_3PMo_{12}O_{40}$ from solution, EtOH was removed under vacuum (rotary evaporator). The solid material (as received or obtained by EtOH removal) was transferred into a Schlenk flask and heated in an oil bath under oil pump vacuum at different temperatures (100 to 130 ºC) for various activation times (1 to 24 h). The resulting solids were transferred into a N_2-filled glovebox for storage.

The resulting solids were evaluated in analogy to General Procedure A, reacting preactivated heteropolyacid (5.0 mol %), $BiCl_3$ (10.0 mg, 0.0318 mmol, 5.0 mol %), and 1-octanol (0.100 ml, 82.7 mg, 0.635 mmol, 1.00 equiv) in PhBr (1.0 mL). The resulting data (see Table 1) show that the highest dehydration activity was achieved for heteropolyacids that had been activated for 2 h at 100 ºC under oil pump vacuum. Thus, all heteropolyacids used in this study were treated accordingly before use in catalysis.

Table 1. Results of Preactivation Study for Various Heteropolyacids. Conditions: heteropolyacid (5.0 mol %), $BiCl_3$ (10.0 mg, 0.0318 mmol, 5.0 mol %), 1-octanol (0.100 ml, 82.7 mg, 0.635 mmol, 1.00 equiv), PhBr (1.0 mL), 125 ºC, 48 h.

Preactivation conditions	% GC Yield Octenes (Ratio 1-/2-/3-Octene)	% GC Yield Dioctyl Ether
$H_3PMo_{12}O_{40}$		
100 ºC, 1 h	7.1 ± 0.2 (0:0.5:1)	20.5 ± 0.8
100 ºC, 2 h	**7.5 ± 0.2 (0:0.5:1)**	**21 ± 1**
100 ºC, 6 h	7 ± 5 (0:0.4:1)	19.1 ± 0.5
130 ºC, 2 h	7.0 ± 0.4 (0:0.5:1)	17.9 ± 0.8
130 ºC, 4 h	6 ± 1 (0:0.5:1)	15.4 ± 0.7
$H_3PW_{12}O_{40}$		
100 ºC, 1 h	8.4 ± 0.6 (0:0.4:1)	21 ± 1
100 ºC, 2 h	**8.5 ± 0.6 (0:0.5:1)**	**23.0 ± 0.7**
100 ºC, 6 h	8.3 ± 0.6 (0:0.5:1)	21 ± 1
130 ºC, 2 h	6 ± 2 (0:0.5:1)	19.3 ± 0.1
130 ºC, 4 h	5 ± 1 (0:0.5:1)	23.2 ± 0.0
$H_4SiW_{12}O_{40}$		
100 ºC, 1 h	1.4 ± 0.6 (0.08:1:0)	14 ± 1
100 ºC, 2 h	**9.0 ± 0.1 (0.04:0.2:1)**	**16 ± 1**
100 ºC, 6 h	3 ± 1 (0.05:0.6:1)	17 ± 1
130 ºC, 2 h	7 ± 2 (0.04:0.4:1)	17.0 ± 0.4
130 ºC, 4 h	8 ± 1 (0.02:0.3:1)	17 ± 0.2

Procedure and Data for Co-Catalyst and Heteropolyacid Screening in Organic Solvents

All reactions were performed according to General Procedure A, reacting reacting preactivated heteropolyacid (5.0 mol %), co-catalyst (5.0 mol %), and 1-octanol (0.100 ml; 82.7 mg; 0.635 mmol; 1.00 equiv) in PhCl or PhBr (1.0 mL). The heteropolyacid had been pre-activated for 2 h at 100 ºC under oil pump vacuum and was stored in the glovebox under N_2 atmosphere prior to use.

Workup and analysis were performed as described in General Procedure A, using PhOAc as internal GC standard. The results of these reactions are given in Table 2 to Table 7 below.

Table 2. Calibrated GC Yields of Co-Catalyst Screening with $H_3PMo_{12}O_{40}$ in PhCl. Conditions: $H_3PMo_{12}O_{40}$ (58.0 mg, 31.8 µmol, 5.0 mol %), co-catalyst (5.0 mol %), 1-octanol (0.100 ml, 82.7 mg, 0.635 mmol, 1.00 equiv), PhCl (1.0 mL), 125 ºC, 48 h.

Co-catalyst	1-Octene [%]	2-Octene [%]	3-Octene [%]	Dioctyl Ether [%]
none	0	0	0.5 ± 0.0	10 ± 5
$Cu(NO_3)_2$	**0**	**3.0 ± 0.1**	**6.5 ± 0.5**	**16.5 ± 0.3**
$Cu(OAc)_2$	0	0	0	1.5 ± 0.2
CuCl	0	0.1 ± 0.0	0.5 ± 0.3	3.0 ± 0.1
$CuSO_4$	**0**	**3.2 ± 0.7**	**6 ± 1**	**16 ± 1**
$CuBr_2$	**0**	**2.2 ± 0.4**	**4 ± 1**	**18.9 ± 0.1**
CuI	0	1.9 ± 0.6	4 ± 1	20 ± 2
$FeSO_4$	0	0	0	2.6 ± 0.1
$FeBr_2$	0	1.4 ± 0.2	2.3 ± 0.7	18 ± 1
$FeCl_3$	0	1.4 ± 0.7	3 ± 1	18 ± 1
$Fe(NO_3)_3$	0.4 ± 0.2	1.4 ± 0.8	3.0 ± 0.2	19 ± 2
$NiBr_2$	0	0.5 ± 0.3	1.3 ± 0.5	14.7 ± 0.2
NiI_2	0	0.4 ± 0.1	1.1 ± 0.3	14 ± 1
$NiSO_4$	0	0	0	3 ± 1
$Ni(NO_3)_2$	0.2 ± 0.0	1.6 ± 0.4	2 ± 1	13 ± 1
$Ni(OTf)_2$	0	0	0	1.1 ± 0.2
BiI_3	0	0.9 ± 0.1	2.1 ± 0.4	17 ± 1
$BiBr_3$	0	0	0	1.6 ± 0.2
$BiCl_3$	**0.1 ± 0.0**	**1.7 ± 0.4**	**3.7 ± 0.4**	**16.1 ± 0.6**
$CoBr_2$	**0**	**0.9 ± 0.0**	**1.1 ± 0.2**	**14 ± 1**
$Mn(OAc)_2$	0	2.0 ± 0.1	3.1 ± 0.4	21 ± 2
$ZnBr_2$	0	1.3 ± 0.1	2.4 ± 0.3	16 ± 1
$ZnCl_2$	0	1.6 ± 0.6	4 ± 1	10.9 ± 0.1
$Zn(OTf)_2$	0	0	0	1.7 ± 0.3
$NaNO_3$	0	2 ± 1	3 ± 2	21 ± 0.0
KNO_3	0	0.5 ± 0.4	1.9 ± 0.5	10 ± 1

Table 3. Calibrated GC Yields of Co-Catalyst Screening with $H_3PMo_{12}O_{40}$ in PhBr. Conditions: $H_3PMo_{12}O_{40}$ (58.0 mg, 31.8 μmol, 5.0 mol %), co-catalyst (5.0 mol %), 1-octanol (0.100 ml, 82.7 mg, 0.635 mmol, 1.00 equiv), PhBr (1.0 mL), 125 ºC, 48 h.

Co-catalyst	**1-Octene [%]**	**2-Octene [%]**	**3-Octene [%]**	**Dioctyl Ether [%]**
none	0	0	0.4 ± 0.1	7 ± 1
$Cu(NO_3)_2$	0	0.9 ± 0.2	4 ± 1	24 ± 8
$CuSO_4$	0	0	0.4 ± 0.1	10 ± 2
$Fe(NO_3)_3$	0.1 ± 0.0	0.4 ± 0.1	2 ± 1	24 ± 4
$BiCl_3$	**0**	**1.4 ± 0.4**	**7 ± 2**	**26 ± 1**
$ZnCl_2$	0.2 ± 0.0	1.1 ± 0.4	6 ± 2	36 ± 3

Table 4. Calibrated GC Yields of Co-Catalyst Screening with $H_3PW_{12}O_{40}$ in PhBr. Conditions: $H_3PW_{12}O_{40}$ (91.6 mg, 31.8 µmol, 5.0 mol %), co-catalyst (5.0 mol %), 1-octanol (0.100 ml; 82.7 mg; 0.635 mmol; 1.00 equiv), PhBr (1.0 mL), 125 ºC, 48 h.

Co-catalyst	1-Octene [%]	2-Octene [%]	3-Octene [%]	Dioctyl Ether [%]
none	0	3 ± 1	9.0 ± 0.6	28.2 ± 0.2
$Cu(NO_3)_2$	0	3 ± 1	5 ± 3	10 ± 2
$Cu(OAc)_2$	**0**	**4 ± 1**	**9 ± 3**	**27 ± 2**
$CuCl_2$	**0**	**4.6 ± 0.2**	**9.9 ± 0.5**	**29 ± 2**
CuCl	0	4 ± 1	8 ± 2	32 ± 3
$Cu(OTf)_2$	**0**	**7.3 ± 0.7**	**16 ± 2**	**17 ± 1**
$CuSO_4$	0	3.2 ± 0.6	7 ± 2	23 ± 1
$CuBr_2$	**0**	**4.4 ± 0.7**	**10.6 ± 0.6**	**28.7 ± 0.5**
CuI	0	3.3 ± 0.3	6.6 ± 0.6	23 ± 1
$FeSO_4$	0	3 ± 1	7.0 ± 0.5	22 ± 1
$FeBr_2$	0	0.2 ± 0.0	0	3.4 ± 0.5
$FeCl_3$	0	1.4 ± 0.7	3 ± 2	20 ± 2
$Fe(NO_3)_3$	0	3.5 ± 0.4	7.3 ± 0.7	17.6 ± 0.4
$ZnBr_2$	0	1.4 ± 0.4	2.8 ± 0.1	18 ± 3
$ZnCl_2$	0	1.5 ± 0.2	3.0 ± 0.1	16 ± 1
$NiBr_2$	0	0.2 ± 0.2	0	3 ± 2
NiI_2	0	2.0 ± 0.7	5 ± 2	18 ± 3
$NiSO_4$	0	2 ± 1	3.3 ± 0.0	31 ± 1
$Ni(NO_3)_2$	0	2 ± 2	5.0 ± 0.3	16 ± 3
$Ni(OTf)_2$	**0**	**4.0 ± 0.7**	**9 ± 2**	**23 ± 2**
BiI_3	0	2.2 ± 0.3	4.3 ± 0.6	33 ± 0.0
$BiBr_3$	0	3.1 ± 0.2	6.8 ± 0.7	25 ± 2
$BiCl_3$	0	2.7 ± 0.2	5.8 ± 0.6	23.0 ± 0.7
$CoBr_2$	**0.4 ± 0.1**	**4.5 ± 0.4**	**9.2 ± 0.9**	**31.5 ± 0.2**
$NaNO_3$	0	3.1 ± 0.6	6 ± 1	26 ± 4
KNO_3	**0**	**5 ± 1**	**12 ± 4**	**25 ± 5**
$Co(NO_3)_2$	**0**	**4.6 ± 0.6**	**10 ± 1**	**20 ± 2**
$Mn(OAc)_2$	**0**	**5.5 ± 0.4**	**12 ± 1**	**30 ± 3**

Table 5. Calibrated GC Yields of Co-Catalyst Screening with $H_3PW_{12}O_{40}$ in PhCl. Conditions: $H_3PW_{12}O_{40}$ (91.6 mg, 31.8 µmol, 5.0 mol %), co-catalyst (5.0 mol %), 1-octanol (0.100 ml; 82.7 mg; 0.635 mmol; 1.00 equiv), PhCl (1.0 mL), 125 ºC, 48 h.

Co-catalyst	1-Octene [%]	2-Octene [%]	3-Octene [%]	Dioctyl Ether [%]
none	**0**	**2 ± 1**	**6.2 ± 0.4**	**31.1 ± 0.5**
$Cu(OAc)_2$	0	0	0.1 ± 0.1	1.4 ± 1.2
$CuCl_2$	0	0.2 ± 0.0	0.6 ± 0.1	19 ± 1
$CuBr_2$	0	0	0.1 ± 0.0	12 ± 2
$Ni(OTf)_2$	0	0	0.1 ± 0.0	11 ± 1
$CoBr_2$	0.2 ± 0.1	0.3 ± 0.0	2.3 ± 0.4	20 ± 1
$Co(NO_3)_2$	0	0.1 ± 0.0	0.4 ± 0.2	7 ± 4
KNO_3	0	0.8 ± 0.4	3 ± 2	44 ± 12
$Mn(OAc)_2$	**0**	**1.9 ± 0.4**	**10 ± 1**	**30 ± 10**

Table 6. Calibrated GC Yields of Co-Catalyst Screening with $H_4SiW_{12}O_{40}$ in PhBr. Conditions: $H_4SiW_{12}O_{40}$ (91.5 mg, 31.8 µmol, 5.0 mol %), co-catalyst (5.0 mol %), 1-octanol (0.100 ml, 82.7 mg, 0.635 mmol, 1.00 equiv), PhBr (1.0 mL), 125 ºC, 48 h.

Co-catalyst	**1-Octene [%]**	**2-Octene [%]**	**3-Octene [%]**	**Dioctyl Ether [%]**
none	0	4.6 ± 0.3	10.7 ± 0.5	25 ± 1
$CuCl_2$	0	4 ± 1	10 ± 2	22 ± 3
$Cu(OTf)_2$	**0**	**5 ± 1**	**12 ± 2**	**18 ± 1**
$Cu(OAc)_2$	0.2 ± 0.0	3.4 ± 0.2	6.7 ± 0.4	28 ± 1
CuCl	0	3.3 ± 0.8	8.1 ± 0.8	22 ± 2
$CuBr_2$	0	2.6 ± 0.6	5 ± 1	33 ± 2
CuI	0	4.6 ± 0.4	9 ± 1	37.5 ± 0.6
$FeSO_4$	0.6 ± 0.1	4.5 ± 0.7	10 ± 2	30 ± 2
$FeBr_2$	0.2 ± 0.0	2.1 ± 0.4	5.5 ± 0.8	15 ± 1
$Fe(OTf)_3$	**0.6 ± 0.1**	**6.0 ± 0.3**	**13.3 ± 0.9**	**21.7 ± 0.1**
$Fe(NO_3)_3$	0	4.7 ± 0.0	10.3 ± 0.3	19 ± 1
$NiCl_2$	0	2.6 ± 0.3	6 ± 1	21 ± 2
$Ni(OTf)_2$	**0**	**5.9 ± 0.6**	**14 ± 1**	**21 ± 3**
$BiCl_3$	0	1.4 ± 0.5	3.2 ± 1.0	16.9 ± 1.6
$CoBr_2$	**0**	**5.0 ± 0.0**	**12.5 ± 0.3**	**26 ± 2**
$Zn(OTf)_2$	**0**	**6.0 ± 0.7**	**13 ± 2**	**24 ± 6**

Table 7. Calibrated GC Yields of Co-Catalyst Screening with $H_4SiW_{12}O_{40}$ in PhCl. Conditions: $H_4SiW_{12}O_{40}$ (91.5 mg, 31.8 µmol, 5.0 mol %), Co-catalyst (5.0 mol %), 1-octanol (0.100 ml, 82.7 mg, 0.635 mmol, 1.00 equiv), PhCl (1.0 mL), 125 ºC, 48 h.

Co-catalyst	**1-Octene [%]**	**2-Octene [%]**	**3-Octene [%]**	**Dioctyl Ether [%]**
none	0.1 ± 0.0	1.9 ± 0.5	3 ± 1	28.2 ± 0.4
$Cu(OTf)_2$	0.1 ± 0.0	0.3 ± 0.0	1.4 ± 0.0	29 ± 8
$Fe(OTf)_3$	**0.1 ± 0.0**	**2.3 ± 0.1**	**11 ± 1**	**38 ± 2**
$Ni(OTf)_2$	**0.8 ± 0.1**	**2.8 ± 0.1**	**13 ± 1**	**32 ± 7**
$CoBr_2$	0.2 ± 0.1	1.5 ± 0.3	7 ± 2	42 ± 2
$Zn(OTf)_2$	0.4 ± 0.0	2.2 ± 0.6	0	37 ± 1

General Procedure B: 1-Octanol Dehydration in Ionic Liquids

Preactivated heteropolyacid (5.0 mol %), metal co-catalyst (5.0 mol %), and ionic liquid (1.0 g) were added to a 4 mL scintillation vial equipped with a Teflon-coated stirbar under N_2 atmosphere (glovebox). After removing the vial from the glovebox, co-solvent (0.10 mL; dried over 4Å MS before use) and 1-octanol (0.100 ml, 82.7 mg, 635 µmol, 1.00 equiv) were added to the mixture.

The vial was sealed with a Teflon-lined cap and heated to 125 °C on a pre-heated vial plate under vigorous stirring (1500 rpm). After the reaction time was completed the vial was taken off the heating block and the mixture was allowed to cool until still slightly warm to the touch (~2 min at room temperature). 10 µL PhOAc were added as GC-standard, followed by DI water (3 mL), diethyl ether (1 mL), and 1 mL of saturated aqueous K_2CO_3 solution to quench the acid. The organic phase was separated, filtered through celite, and analyzed by calibrated gas chromatography.

Ionic Liquid Screening for 1-Octanol Dehydration

In analogy to General Procedure B, preactivated $H_3PW_{12}O_{40}$ (91.6 mg, 31.8 µmol, 5.0 mol %), $BiCl_3$ (10.0 mg, 31.8 µmol, 5.0 mol %), ionic liquid (1.0 g), para-xylene (0.10 mL; dried over 4Å MS before use), and 1-octanol (0.100 ml, 82.7 mg, 635 µmol, 1.00 equiv) were reacted for 48 h at 125 °C. Workup and analysis were performed as described in General Procedure B, resulting in the yields shown in Table 8.

Table 8. Calibrated GC Yields for Ionic Liquid Screening. Conditions: $H_3PW_{12}O_{40}$ (91.6 mg, 31.8 µmol, 5.0 mol %), $BiCl_3$ (10.0 mg, 31.8 µmol, 5.0 mol %), 1-octanol (0.100 ml, 82.7 mg, 635 µmol, 1.00 equiv), ionic liquid (1.0 g), para-xylene (0.10 mL), 125 ºC, 48 h.

Ionic Liquid	**1-Octene [%]**	**2-Octene [%]**	**3-Octene [%]**	**Dioctyl Ether [%]**
[bmim]Cl	**2.6 ± 0.0**	**0**	**0**	**1.9 ± 0.0**
[bmim]O_3SCF_3	0	0	0	1.8 ± 0.6
[emim]Cl	0.4 ± 0.0	0	0	1.5 ± 0.8
[emim]Br	**2.3 ± 0.6**	**0**	**0**	**6.6 ± 0.4**
[NBu_4]O_3SCF_3	0.5 ± 0.2	0.7 ± 0.0	0.3 ± 0.0	26 ± 3
[NBu_4]Br	**4.0 ± 0.6**	**0**	**0**	**3.6 ± 0.6**
[NBu_4]OAc	0	0	0	0
[NBu_4]O_3SMe	0	0	0	0
[$NHex_4$]Br	0	0.2 ± 0.0	0.5 ±0.0	1.8 ± 0.1
[$NHex_4$]I	0	0.6 ± 0.1	0	0.2 ± 0.1
[NBu_3Me]Cl	0	0	0	0
Choline chloride/ urea 1:2[1]	0	0	0	0
Choline chloride/ acetamide 1:2[1]	0	0	0	0

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[1] A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed, V. Tambyrajah, *Chem.Commun.* **2003**, 70-71.

Co-Solvent Screening for 1-Octanol Dehydration in NBu_4Br

In analogy to General Procedure B, preactivated $H_3PW_{12}O_{40}$ (91.6 mg, 31.8 µmol, 5.0 mol %), $BiCl_3$ (10.0 mg, 31.8 µmol, 5.0 mol %), NBu_4Br (1.00 g, 3.10 mmol, 4.88 equiv), co-solvent (0.10 mL; dried over 4Å MS before use), and 1-octanol (0.100 ml, 82.7 mg, 635 µmol, 1.00 equiv) were reacted for 48 h at 125 °C. Workup and analysis were performed as described in General Procedure B; obtained GC yields are shown in Table 9.

Table 9. Calibrated GC Yields for Co-Solvent Screening. Conditions: $H_3PW_{12}O_{40}$ (91.6 mg, 31.8 µmol, 5.0 mol %), $BiCl_3$ (10.0 mg, 31.8 µmol, 5.0 mol %), 1-octanol (0.100 ml, 82.7 mg, 635 µmol, 1.00 equiv), NBu_4Br (1.00 g, 3.10 mmol, 4.88 equiv), co-solvent (0.10 mL), 125 ºC, 48 h.

Co-Solvent	1-Octene [%]	2-Octene [%]	3-Octene [%]	Dioctyl Ether [%]
PhCl	**3.7 ± 0.4**	**0**	**0**	**3.8 ± 0.3**
PhBr	2.8 ± 0.1	0	0	2.7 ± 0.0
***para*-xylene**	**4.0 ± 0.6**	**0**	**0**	**3.6 ± 0.6**
Decalin	0.5 ± 0.1	0	0	0.5 ± 0.2
Decane	0	0	0	9 ± 2
Butyl Ether	0	0	0	5.7 ± 0.7
DMA	0	0	0	2.5 ± 0.6
DMF	**3.7 ± 0.5**	**0**	**0**	**4.8 ± 0.1**

Co-Catalyst/Acid Screening for 1-Octanol Dehydration in NBu_4Br

In analogy to General Procedure B, preactivated $H_3PW_{12}O_{40}$ (91.6 mg, 31.8 µmol, 5.0 mol %), co-catalyst (5.0 mol %), NBu_4Br (1.00 g, 3.10 mmol, 4.88 equiv), *para*-xylene (0.10 mL; dried over 4Å MS before use), and 1-octanol (0.100 ml, 82.7 mg, 635 µmol, 1.00 equiv) were reacted for 48 h at 125 °C. Workup and analysis were performed as described in General Procedure B, resulting in the yields shown in Table 10.

Table 10. Calibrated GC Yields for Co-Catalyst Screening with $H_3PW_{12}O_{40}$. Conditions: $H_3PW_{12}O_{40}$ (91.6 mg, 31.8 µmol, 5.0 mol %), co-catalyst (5.0 mol %), 1-octanol (0.100 ml, 82.7 mg, 635 µmol, 1.00 equiv), NBu_4Br (1.00 g, 3.10 mmol, 4.88 equiv), *para*-xylene (0.10 mL), 125 ºC, 48 h.

Co-Catalyst	1-Octene [%]	2-Octene [%]	3-Octene [%]	Dioctyl Ether [%]
$BiCl_3$	4.0 ± 0.6	0	0	3.6 ± 0.6
$Cu(OTf)_2$	**21 ± 3**	**15 ± 2**	**6 ± 1**	**12 ± 1**
$CuBr_2$	**23 ± 4**	**11 ± 4**	**7 ± 1**	**12 ± 6**
$Fe(NO_3)_2$	7 ± 1	0.1 ± 0.0	0	27 ± 4
$Fe(OTf)_3$	0	0	0	0.6 ± 0.1
$Ni(OTf)_2$	0	0	0.1 ± 0.0	0.3 ± 0.0
$CoBr_2$	2.1 ± 0.3	0	0	10 ± 1
$Mn(OAc)_2$	0.7 ± 0.0	0	0	2.3 ± 0.1
$Co(NO_3)_2$	**25 ± 1**	**3.0 ± 0.1**	**0.9 ± 0.1**	**34 ± 3**
KNO_3	0	0	2 ± 1	7 ± 2
$Zn(OTf)_2$	0	0	2 ± 1	4.8 ± 0.0
none	0.1 ± 0.0	0.2 ± 0.0	0	0.6 ± 0.0

Table 11. Calibrated GC Yields for Co-Catalyst Screening with $H_4SiW_{12}O_{40}$ in NBu_4Br. Conditions: $H_4SiW_{12}O_{40}$ (91.5 mg, 31.8 µmol, 5.0 mol %), co-catalyst (5.0 mol %), 1-octanol (0.100 ml, 82.7 mg, 635 µmol, 1.00 equiv), NBu_4Br (1.00 g, 3.10 mmol, 4.88 equiv), *para*-xylene (0.10 mL), 125 ºC, 48 h.

Co-catalyst	**1-Octene [%]**	**2-Octene [%]**	**3-Octene [%]**	**Dioctyl Ether [%]**
$BiCl_3$	10 ± 1	0	1.1 ± 0.3	14 ± 2
$Cu(OTf)_2$	**15 ± 1**	**22 ± 4**	**11 ± 3**	**7.2 ± 0.4**
$CuBr_2$	**14 ± 2**	**23 ± 2**	**12 ± 2**	**7 ± 2**
CuI	23 ± 0	15 ± 2	6 ± 1	13 ± 1
$Fe(OTf)_3$	5 ± 2	0.6 ± 0.4	0	20 ± 4
$Ni(OTf)_2$	18 ± 2	13 ± 1	3.4 ± 0.6	12 ± 2
$CoBr_2$	15 ± 2	14 ± 0	4.1 ± 0.4	7 ± 2
$Co(NO_3)_2$	16 ± 1	10 ± 1	2.4 ± 0.3	12 ± 0
$Zn(OTf)_2$	17 ± 1	15 ± 2	4 ± 1	10 ± 2
KBr	19 ± 3	16 ± 3	5 ± 2	12 ± 3
NaBr	20 ± 3	16 ± 0	5 ± 1	11 ± 1
NaI	26 ± 0	15 ± 3	4 ± 1	17 ± 3
none	19 ± 0	15 ± 0	4.0 ± 0.2	10 ± 1

Optimization of Co-Solvent Volume for 1-Octanol Dehydration in NBu_4Br

In analogy to General Procedure B, preactivated $H_4SiW_{12}O_{40}$ (91.5 mg, 31.8 µmol, 5.0 mol %), $CuBr_2$ (7.1 mg, 32 µmol, 5.0 mol %), NBu_4Br (1.00 g, 3.10 mmol, 4.88 equiv), *para*-xylene (0 to 1.0 mL; dried over 4Å MS before use), and 1-octanol (0.100 ml, 82.7 mg, 635 µmol, 1.00 equiv) were reacted for 48 h at 125 °C. Workup and analysis were performed as described in General Procedure B, resulting in the yields shown in Table 12.

Table 12. Calibrated GC Yields for Screening Different Volumes of para-Xylene as Co-Solvent. Conditions: $H_4SiW_{12}O_{40}$ (91.5 mg, 31.8 µmol, 5.0 mol %), $CuBr_2$ (7.1 mg, 32 µmol, 5.0 mol %), 1-octanol (0.100 ml, 82.7 mg, 635 µmol, 1.00 equiv), NBu_4Br (1.00 g, 3.10 mmol, 4.88 equiv), *para*-xylene (0 to 1.0 mL), 125 ºC, 48 h.

Volume *p*-Xylene [mL]	**1-Octene [%]**	**2-Octene [%]**	**3-Octene [%]**	**Dioctyl Ether [%]**	**Total Olefin [%]**
0	11 ± 1	17 ± 1	10 ± 1	2.6 ± 0.6	38 ± 2
0.05	10 ± 0	21 ± 0	13 ± 0	2.4 ± 0.6	44 ± 0
0.10	**14 ± 2**	**23 ± 2**	**12 ± 2**	**7 ± 2**	**49 ± 2**
0.15	16 ± 1	19 ± 1	8 ± 1	8 ± 1	43 ± 2
0.20	18 ± 0	15 ± 2	5 ± 1	12 ± 1	38 ± 2
0.50	14 ± 2	1.3 ± 0.4	0.1 ± 0.0	21 ± 2	15 ± 2
1.0	4.5 ± 0.3	0	0	9.8 ± 0.2	5 ± 1

Temperature Study

In analogy to General Procedure B, preactivated $H_4SiW_{12}O_{40}$ (91.5 mg, 31.8 µmol, 5.0 mol %), $CuBr_2$ (7.1 mg, 32 µmol, 5.0 mol %), NBu_4Br (1.00 g, 3.10 mmol, 4.88 equiv), *para*-xylene (0.10 mL; dried over 4Å MS before use), and 1-octanol (0.100 ml, 82.7 mg, 635 µmol, 1.00 equiv) were reacted for 48 h at varying temperatures. Workup and analysis were performed as described in General Procedure B, resulting in the yields shown in Table 13.

Table 13. Calibrated GC Yields for Temperature Study. Conditions: $H_4SiW_{12}O_{40}$ (91.5 mg, 31.8 µmol, 5.0 mol %), $CuBr_2$ (7.1 mg, 32 µmol, 5.0 mol %), 5.0 mol %), 1-octanol (0.100 ml, 82.7 mg, 635 µmol, 1.00 equiv), NBu_4Br (1.00 g, 3.10 mmol, 4.88 equiv), *para*-xylene (0.10 mL), 48 h.

Temperature [ºC]	**1-Octene [%]**	**2-Octene [%]**	**3-Octene [%]**	**Dioctyl Ether [%]**
140	10 ± 3	6 ± 2	1.3 ± 0.6	11 ± 1
130	13 ± 3	10 ± 1	5 ± 2	10 ± 1
125	**14 ± 2**	**23 ± 2**	**12 ± 2**	**7 ± 2**
120	14 ± 1	19 ± 2	9 ± 2	7 ± 3
110	16 ± 1	9.5 ± 0.4	2.1 ± 0.2	14 ± 2
100	0 ± 0	0.13 ± 0.03	7 ± 1	16 ± 4
90	0	0	0	0

Time Study for 1-Octanol Dehydration with $H_4SiW_{12}O_{40}$ and $CuBr_2$

In analogy to General Procedure B, preactivated $H_4SiW_{12}O_{40}$ (91.5 mg, 31.8 µmol, 5.0 mol %), $CuBr_2$ (7.1 mg, 32 µmol, 5.0 mol %), NBu_4Br (1.00 g, 3.10 mmol, 4.88 equiv), *para*-xylene (0.10 mL; dried over 4Å MS before use), and 1-octanol (0.100 ml, 82.7 mg, 635 µmol, 1.00 equiv) were reacted for varying reaction times at 125 °C. Workup and analysis were performed as described in General Procedure B, resulting in the yields shown in Table 14.

Table 14. Calibrated GC Yields for Time Study. Conditions: $H_4SiW_{12}O_{40}$ (91.5 mg, 31.8 µmol, 5.0 mol %), $CuBr_2$ (7.1 mg, 32 µmol, 5.0 mol %), 1-octanol (0.100 ml, 82.7 mg, 635 µmol, 1.00 equiv), NBu_4Br (1.00 g, 3.10 mmol, 4.88 equiv), *para*-xylene (0.10 mL), 48 h.

Time [h]	**1-Octene [%]**	**2-Octene [%]**	**3-Octene [%]**	**Dioctyl Ether [%]**	**1-Bromo-octane [%]**	**1-Octanol [%]**	**Mass Balance [%]^a**
0.17	0.03±0.01	0	0	0.5 ± 0.1	18 ± 1	73 ± 6	92 ± 6
2	3.5 ± 0.2	0.1 ± 0.1	0	5 ± 1	18 ± 1	63 ± 5	95 ± 5
6	8.9 ± 0.4	1.2 ± 0.1	0.2 ± 0.0	9.3 ± 0.6	17 ± 1	49 ± 4	95 ± 4
10	17 ± 1	6 ± 1	1.0 ± 0.3	17 ± 1	12 ± 1	23 ± 6	93 ± 6
24	19 ± 1	13 ± 2	3 ± 1	12 ± 2	11 ± 1	18 ± 5	88 ± 6
48	14 ± 2	23 ± 2	12 ± 2	7 ± 2	6.4 ± 0.3	6 ± 2	75 ± 5
72	0	0.2 ± 0.0	0.5 ± 0.1	2.0 ± 0.4	0.42 ± 0.2	6 ± 2	9 ± 2

[a]Values for mass balance are obtained by addition of all values of substrates and products. Standard deviations in the last column are obtained as $std_{mass\ balance} = \sqrt{std_{1-octene} + std_{2-octene} + std_{3-octene} + std_{Oct2O} + std_{BrOct} + std_{OctOH}}$.[2]

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[2] A. C. Berry, *Transactions of the American Mathematical Society* **1941**, *49*, 122-136.

Effect of Lewis and Bronstedt Acid Catalyst Loadings

In analogy to General Procedure B, preactivated $H_4SiW_{12}O_{40}$ (5.0, 1.0, or 0 mol %), $CuBr_2$ (5.0, 1.0, or 0 mol %), NBu_4Br (1.00 g, 3.10 mmol, 4.88 equiv), *para*-xylene (0.10 mL; dried over 4Å MS before use), and 1-octanol (0.100 ml, 82.7 mg, 635 µmol, 1.00 equiv) were reacted for 48 h at 125 °C. Workup and analysis were performed as described in General Procedure B, resulting in the yields shown in Table 15.

Table 15. Calibrated GC Yields for Time Study.

$H_4SiW_{12}O_{40}$ [mol %]	**$CuBr_2$ [mol %]**	**Yield 1-Octene**	**Yield 2-Octene**	**Yield 3-Octene**	***Total Olefin Yield***	**Yield Oct_2O**
5	5	14%	23%	12%	*49%*	7%
5	1	15%	16%	6%	*37%*	8%
5	0	19%	15%	4%	*38%*	10%
1	5	3%	0%	0%	*3%*	7%
0	5	0%	0%	0%	*0%*	2%

Dependence of Olefin to Ether Ratio on Reaction Volume

In analogy to General Procedure B, preactivated $H_4SiW_{12}O_{40}$ (91.5 mg, 31.8 µmol, 5.0 mol %), NBu_4Br (1.00 or 2.00 g), *para*-xylene (0.10 or 0.20 mL; dried over 4Å MS before use), $CuBr_2$ (7.1 mg, 32 µmol, 5.0 mol %), and 1-octanol (0.100 ml, 82.7 mg, 635 µmol, 1.00 equiv) were reacted for 6 h at 125 °C. Workup and analysis were performed as described in General Procedure B, resulting in the yields shown in

Table 16. Calibrated GC Yields for Reaction Volume Study. Conditions: $H_4SiW_{12}O_{40}$ (91.5 mg, 31.8 µmol, 5.0 mol %), $CuBr_2$ (7.1 mg, 32 µmol, 5.0 mol %), 1-octanol (0.100 ml, 82.7 mg, 635 µmol, 1.00 equiv), NBu_4Br (1.00 g or 2.00 g), *para*-xylene (0.10 or 0.20 mL), 125 °C, 6 h.

1-Octene [%]	2-Octene [%]	3-Octene [%]	Dioctyl Ether [%]	1-Bromooctane [%]
1.0 g NBu_4Br & 0.10 mL p-Xylene				
8.9 ± 0.4	1.2 ± 0.1	0.2 ± 0.0	9.3 ± 0.6	17 ± 1
2.0 g NBu_4Br & 0.10 mL p-Xylene				
13 ± 1	1.4 ± 0.0	0	10 ± 1	18 ± 1
4.0 g NBu_4Br & 0.10 mL p-Xylene				
4 ± 1	0.2 ± 0.0	0.1 ± 0.0	3 ± 1	8 ± 2
1.0 g NBu_4Br & 0.20 mL p-Xylene				
7.6 ± 0.1	0.7 ± 0.0	0.1 ± 0.0	10 ± 1	15 ± 0
1.0 g NBu_4Br & 0.40 mL p-Xylene				
5.8 ± 0.4	0.3 ± 0.0	0	8.2 ± 0.5	14 ± 2
2.0 g NBu_4Br & 0.20 mL p-Xylene				
12 ± 1	1.0 ± 0.1	0.1 ± 0.0	7.7 ± 0.3	16 ± 2

Conversion of 1-Bromooctane under Dehydration Conditions

In analogy to General Procedure B, preactivated $H_4SiW_{12}O_{40}$ (91.5 mg, 31.8 µmol, 5.0 mol %), $CuBr_2$ (7.1 mg, 32 µmol, 5.0 mol %), NBu_4Br (1.00 g, 3.10 mmol, 4.88 equiv), *para*-xylene (0.10 mL; dried over 4Å MS before use), and 1-bromooctane (0.11 ml, 122 mg, 635 µmol, 1.00 equiv) were reacted at 125 °C. Workup and analysis were performed as described in General Procedure B; product yields are tabulated below (Table 17).

Table 17. Calibrated GC Yields for Reaction of 1-Bromooctane versus Time. Conditions: $H_4SiW_{12}O_{40}$ (91.5 mg, 31.8 µmol, 5.0 mol %), $CuBr_2$ (7.1 mg, 32 µmol, 5.0 mol %), 1-octanol (0.100 ml, 82.7 mg, 635 µmol, 1.00 equiv), NBu_4Br (1.00 g, 3.10 mmol, 4.88 equiv), *para*-xylene (0.10 mL), 48 h.

Time [h]	**1-Octene [%]**	**2-Octene [%]**	**3-Octene [%]**	**Dioctyl Ether [%]**	**1-Bromooctane [%]**	**1-Octanol [%]**	**Mass Balance [%][a]**
0.17	0.2 ± 0.1	0.7 ± 0.2	0	0	85 ± 6	0	86 ± 3
1	0.4 ± 0.1	1.2 ± 0.3	3.0 ± 0.2	0	66 ± 3	0	70 ± 2
6	1.0 ± 0.3	11.1 ± 0.4	21.0 ± 0.4	0	34 ± 3	4.2 ± 0.3	71 ± 2
15	0.9 ± 0.1	15 ± 2	29 ± 4	0	8.2 ± 0.7	7.7 ± 0.9	61 ± 3
24	0.9 ± 0.1	16 ± 1	32 ± 2	0	2.9 ± 0.6	7.0 ± 0.9	61 ± 2

[a] Values for mass balance are obtained by addition of all values of substrates and products. Standard deviations in the last column are obtained as $std_{mass\ balance} = \sqrt{std_{1-octene} + std_{2-octene} + std_{3-octene} + std_{Oct2O} + std_{BrOct} + std_{OctOH}}$.[2]

Conversion of 1-Bromooctane/1-Octanol (1:1) under Dehydration Conditions

In analogy to General Procedure B, preactivated $H_4SiW_{12}O_{40}$ (91.5 mg, 31.8 µmol, 5.0 mol %), $CuBr_2$ (7.1 mg, 32 µmol, 5.0 mol %), NBu_4Br (1.00 g, 3.10 mmol, 4.88 equiv), *para*-xylene (0.10 mL; dried over 4Å MS before use), 1-bromooctane (0.55 ml, 61 mg, 318 µmol, 0.50 equiv), and 1-octanol (0.50 ml, 41 mg, 318 µmol, 0.50 equiv) were reacted for 48 h at 125 °C. Workup and analysis were performed as described in General Procedure B, resulting in a mixture of 1-octene (0.7 ± 0.1%),[3] 2-octene (19 ± 3%),[3] 3-octene (36 ± 5%),[3] 1-octanol (9 ± 2%),[3] and 1-bromooctane (0.8 ± 0.3%)[3] without any traces of dioctyl ether as determined by calibrated GC analysis.

Conversion of Dioctyl Ether under Dehydration Conditions

In analogy to General Procedure B, preactivated $H_4SiW_{12}O_{40}$ (91.5 mg, 31.8 µmol, 5.0 mol %), $CuBr_2$ (7.1 mg, 32 µmol, 5.0 mol %), NBu_4Br (1.00 g, 3.10 mmol, 4.88 equiv), *para*-xylene (0.10 mL; dried over 4Å MS before use), and dioctyl ether (95.7 µL, 77.1 mg, 318 µmol, 0.50 equiv) were reacted for 48 h at 125 °C. Workup and analysis were performed as described in General Procedure B, resulting in a mixture of 1-octene (20 ± 1%),[4] 2-octene (18 ± 1%),[4] 3-octene (5.7 ± 0.5%),[4] 1-bromooctane (3.6 ± 0.1%),[4] 1-octanol (3.9 ± 0.5%),[4] and remaining dioctyl ether (12 ± 1%) as determined by calibrated GC analysis.

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[3] These yields were calculated based on 1.00 equiv. of octene building blocks present in 0.50 equiv. 1-octanol and 0.50 equiv. 1-bromooctene.

[4] These yields were calculated based on 1.00 equiv. of octene building blocks present in 0.50 equiv. dioctyl ether.

Isomerization of 1-Octene under Dehydration Conditions

In analogy to General Procedure B, preactivated $H_4SiW_{12}O_{40}$ (91.5 mg, 31.8 µmol, 5.0 mol %), $CuBr_2$ (7.1 mg, 32 µmol, 5.0 mol %), NBu_4Br (1.00 g, 3.10 mmol, 4.88 equiv), *para*-xylene (0.10 mL; dried over 4Å MS before use), and 1-octene (0.100 ml, 71.3 mg, 635 µmol, 1.00 equiv) were reacted for at 125 °C. Workup and analysis were performed as described in General Procedure B, resulting in a mixture of 1-octene, 2-octene, and 3-octene, without any 1-bromooctane, 1-octanol, or dioctyl ether as by-products as determined by calibrated GC analysis.

Table 18. Calibrated GC Yields for Reaction of 1-Octene versus Time. Conditions: $H_4SiW_{12}O_{40}$ (91.5 mg, 31.8 µmol, 5.0 mol %), $CuBr_2$ (7.1 mg, 32 µmol, 5.0 mol %), 1-octanol (0.100 ml, 82.7 mg, 635 µmol, 1.00 equiv), NBu_4Br (1.00 g, 3.10 mmol, 4.88 equiv), *para*-xylene (0.10 mL).

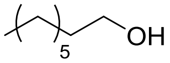
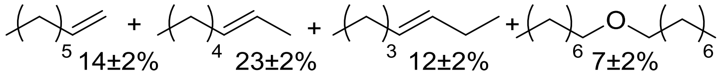
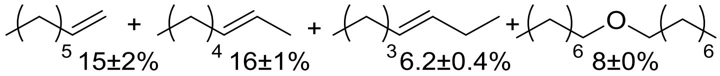
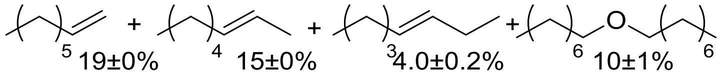
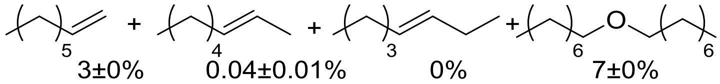
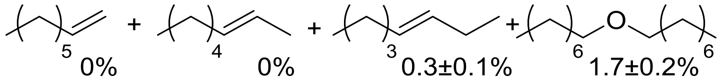
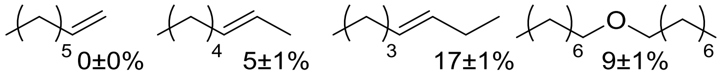
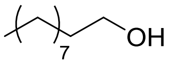
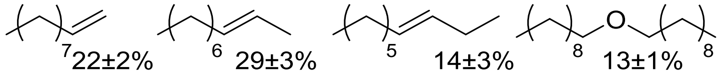
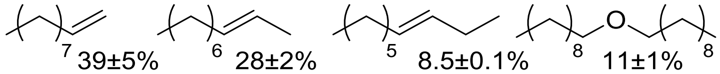
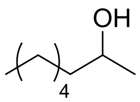
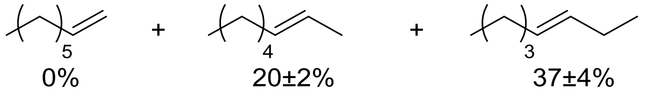
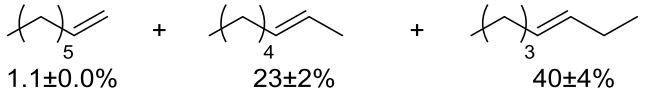
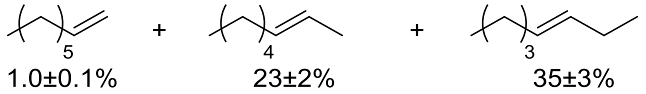
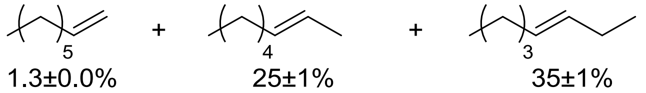
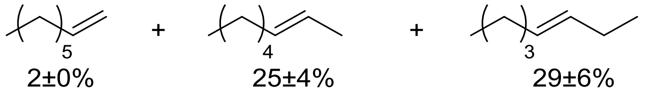
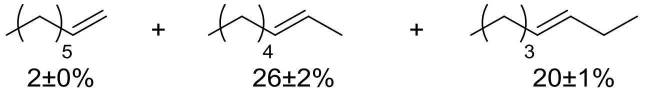
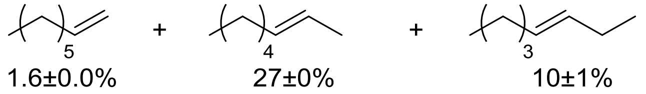
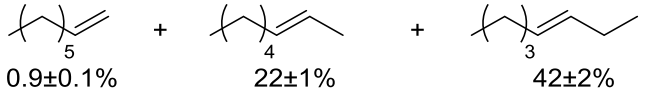
Time [h]	1-Octene [%]	2-Octene [%]	3-Octene [%]
0.17	71 ± 8	22 ± 4	2.3 ± 0.4
1	16 ± 3	31 ± 3	15 ± 1
4	3.5 ± 0.5	34 ± 5	48 ± 7
6	2.2 ± 0.0	30 ± 1	51 ± 3
24	1.3 ± 0.1	21 ± 2	40 ± 3

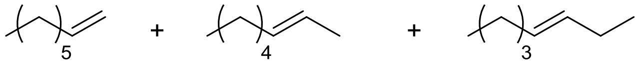
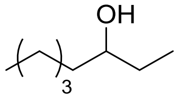
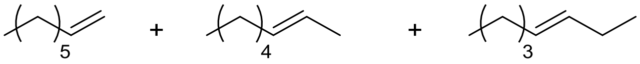
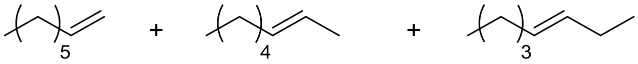
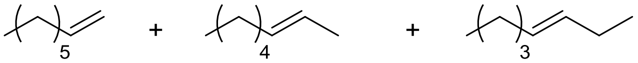
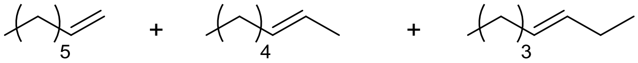
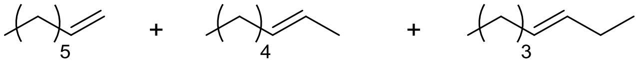
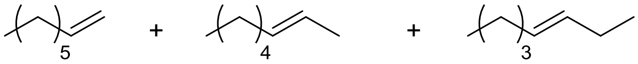
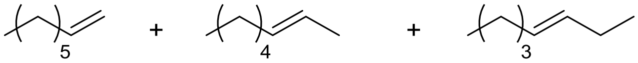
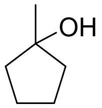
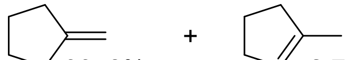
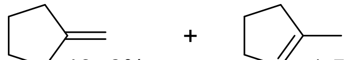
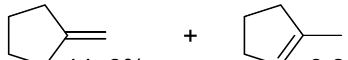
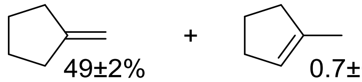
Substrate Scope

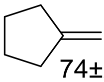
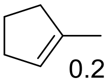
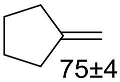
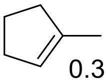
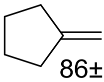
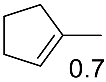
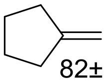
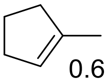
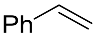
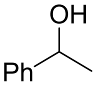
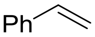
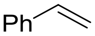
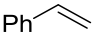
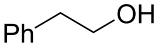
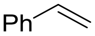
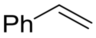
Procedure for Primary, Secondary and Tertiary alcohols

In analogy to General Procedure B, preactivated $H_4SiW_{12}O_{40}$ (91.5 mg, 31.8 µmol, 5.0 mol %), $CuBr_2$ (7.1 mg, 32 µmol, 5.0 mol %), NBu_4Br (1.00 g, 3.10 mmol, 4.88 equiv), *para*-xylene (0.10 mL; dried over 4Å MS before use), and alcohol substrate (635 µmol, 1.00 equiv) were reacted at 125 °C for various reaction times (see Table 19). Workup and analysis were performed as described in General Procedure B and the product yields were determined by calibrated GC analysis, using PhOAc as internal GC standard. The identities of all products were verified by comparison of the obtained data with GC and GC-MS data of original samples (retention times; obtained mass spectra).

Table 19. GC Yields for Substrate Scope Study. Conditions: $H_4SiW_{12}O_{40}$ (91.5 mg, 31.8 µmol, 5.0 mol %), $CuBr_2$ (7.1 mg, 32 µmol, 5.0 mol %), alcohol (635 µmol, 1.00 equiv), NBu_4Br (1.00 g, 3.10 mmol, 4.88 equiv), *para*-xylene (0.10 mL), 125 °C.

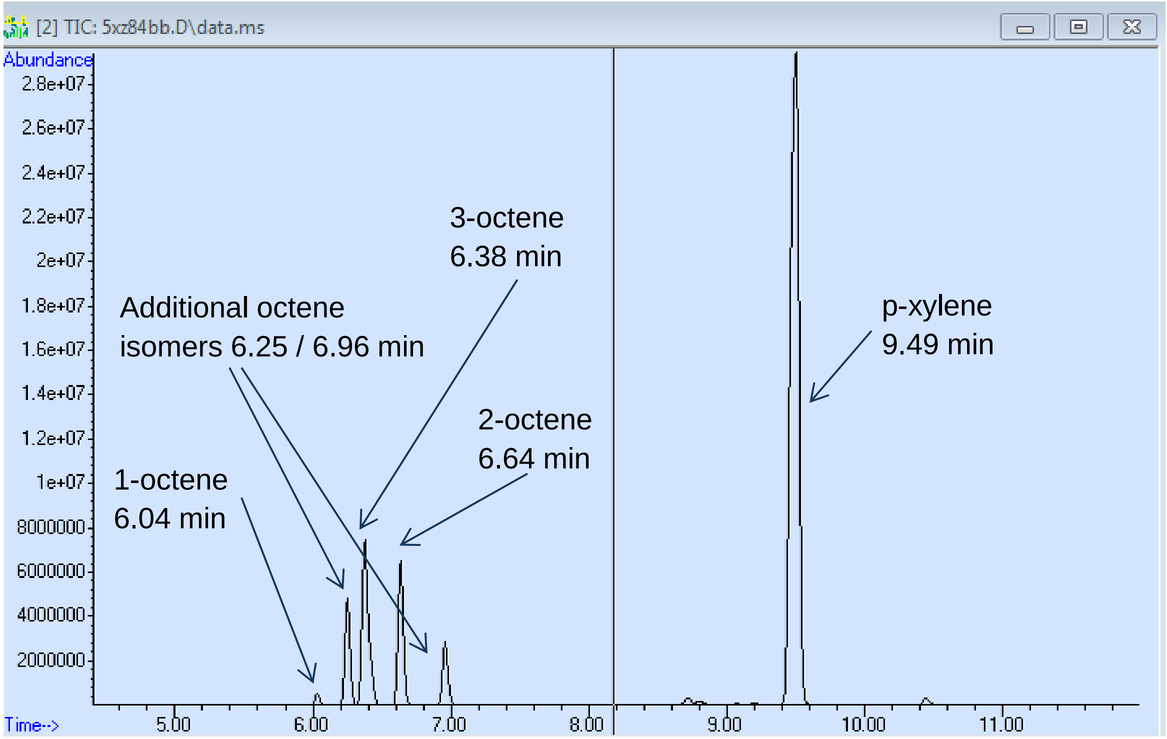
Reaction Time [h]	**Substrate**	**Product(s)**
48		 14±2% + 23±2% + 12±2% + 7±2%
48[a]		 15±2% + 16±1% + 6.2±0.4% + 8±0%
48[b]		 19±0% + 15±0% + 4.0±0.2% + 10±1%
48[c]		 3±0% + 0.04±0.01% + 0% + 7±0%
48[d]		 0% + 0% + 0.3±0.1% + 1.7±0.2%
48[e]		 0±0% 5±1% 17±1% 9±1%
48		 22±2% 29±3% 14±3% 13±1%
48[f]		 39±5% 28±2% 8.5±0.1% 11±1%
48		 0% + 20±2% + 37±4%
24		 1.1±0.0% + 23±2% + 40±4%
8		 1.0±0.1% + 23±2% + 35±3%
6		 1.3±0.0% + 25±1% + 35±1%
4		 2±0% + 25±4% + 29±6%
2		 2±0% + 26±2% + 20±1%
1		 1.6±0.0% + 27±0% + 10±1%
48[b]		 0.9±0.1% + 22±1% + 42±2%

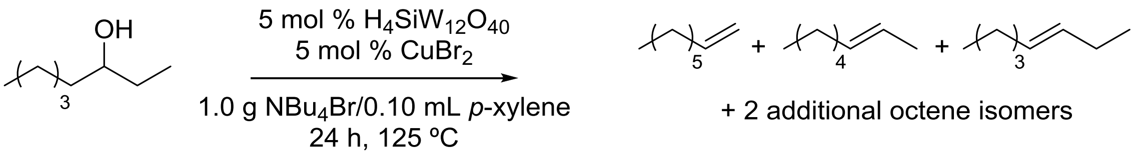
24[b]			1.2±0.0%	23±0%	34±1%
48			0%	22±1%	41±3%
8			1.0±0.1%	21±2%	39±5%
6			1.1±0.0%	26±0%	46±0%
4			1.1±0.0%	25±1%	42±1%
2			0.9±0.1%	24±1%	35±2%
48[b]			0.3±0.1%	8±2%	15±5%
8[b]			1.0±0.2%	21±2%	38±4%
48			33±8%	2.7±0.2%	
24			37±1%	2.5±0.3%	
1			40±6%	1.5±0.3%	
0.5			40±7%	0.8±0.2%	
0.25			44±8%	0.8±0.1%	
48[b]			40±3%	3.1±0.3%	
24[b]			50±3%	2.7±0.5%	
1[b]			58±2%	1.7±0.4%	
0.5[b]			56±5%	0.8±0.2%	
0.25[b]			49±2%	0.7±0.1%	

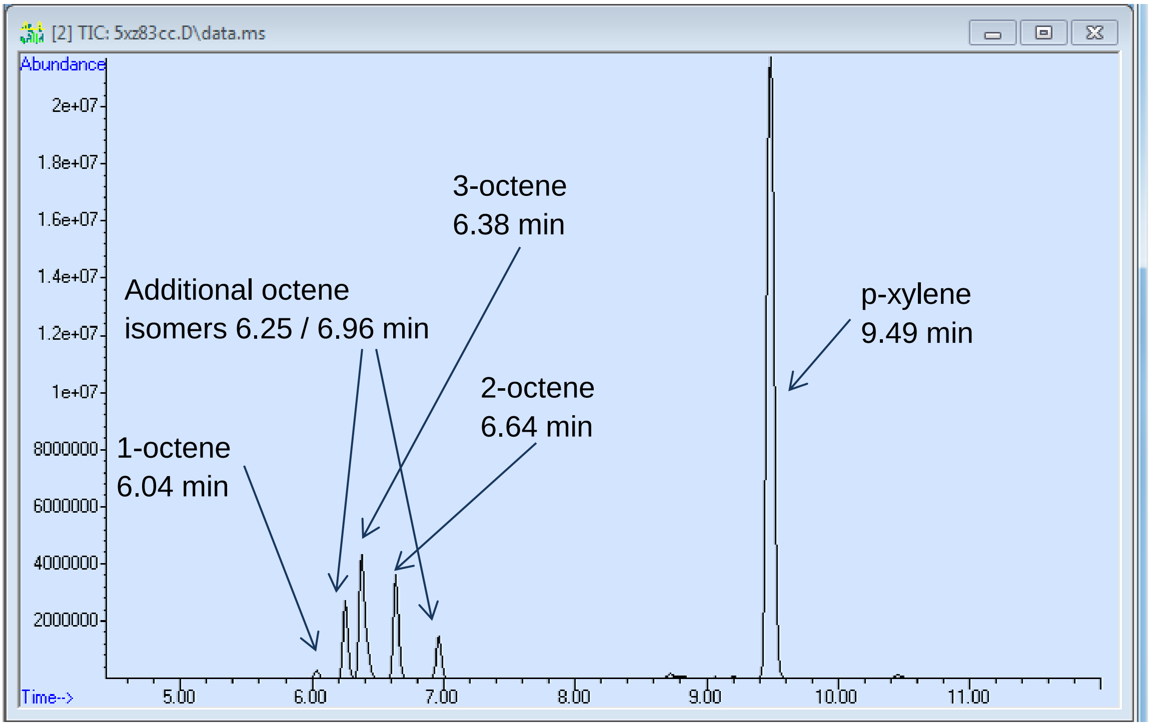
1[g]		 74±2%	+  0.2±0.0%
2[g]		 75±4%	+  0.3±0.0%
1[b,g]		 86±3%	+  0.7±0.0%
2[b,g]		 82±5%	+  0.6±0.0%
48		 0%	
1		 89±1%	
1[b]		 29±1%	
48		 91±6%	
48[b]		 13±2%	
1		 4.2±0.2%	

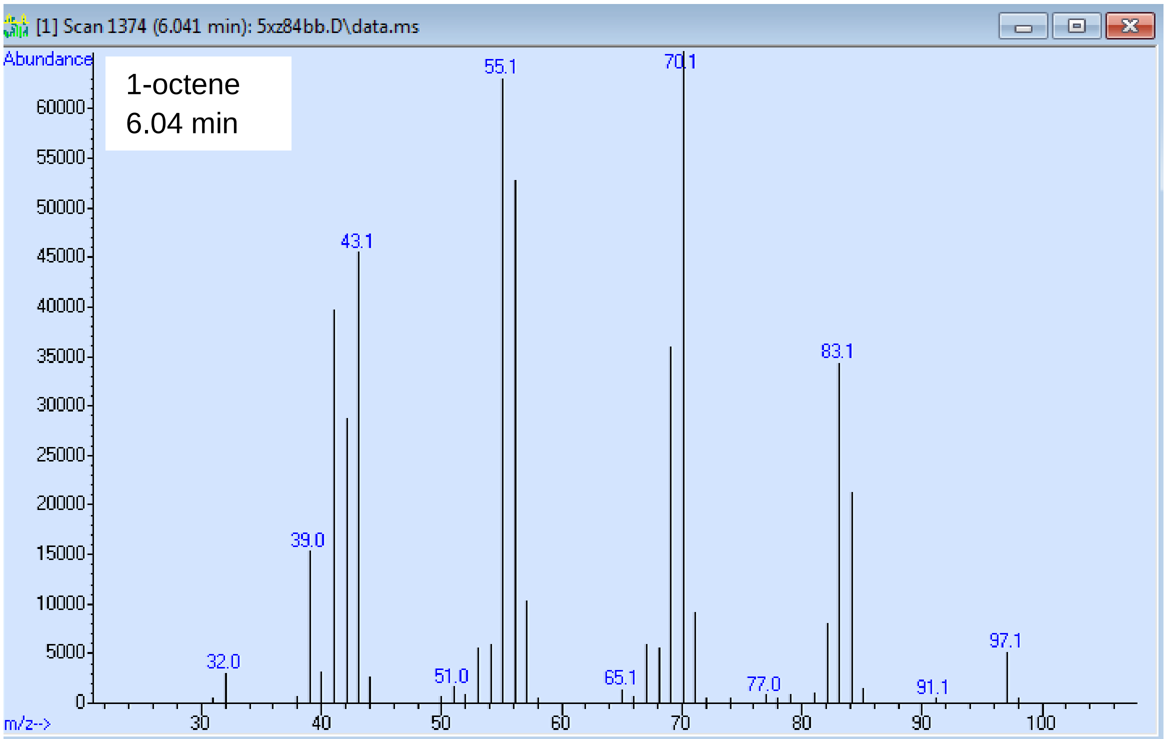
[a] Only 1.0 mol % $CuBr_2$ (1.4 mg, 6.4 µmol) was used. [b] No $CuBr_2$ was used. [c] Only 1.0 mol % $H_4SiW_{12}O_{40}$ (18.4 mg, 6.4 µmol) was used. [d] No $H_4SiW_{12}O_{40}$ was used. [e] 10 mol % $H_4SiW_{12}O_{40}$ (184 mg, 64 µmol) and no $CuBr_2$ was used. [f] 2.0 g NBu_4Br (6.20 mmol, 9.76 equiv) was used. [g] Reaction at 100 °C.

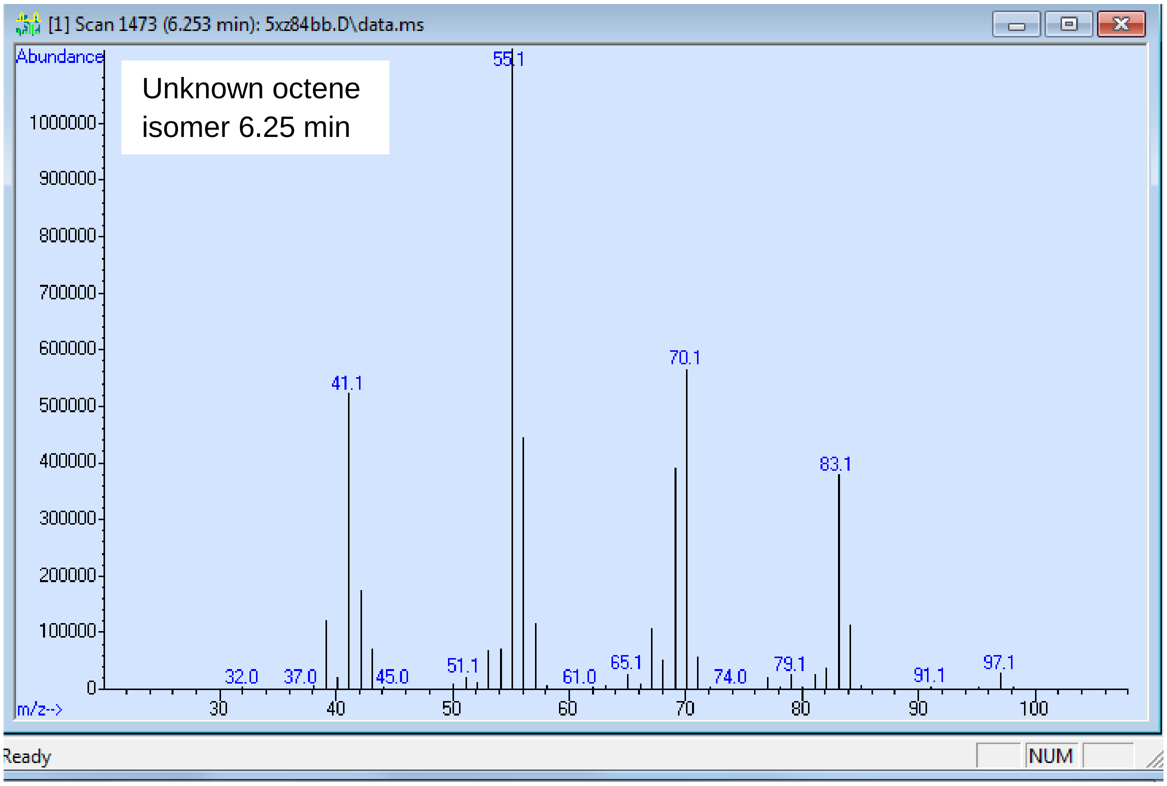
GC-MS Spectra of Octanol Dehydration Showing Additional Octene Isomers

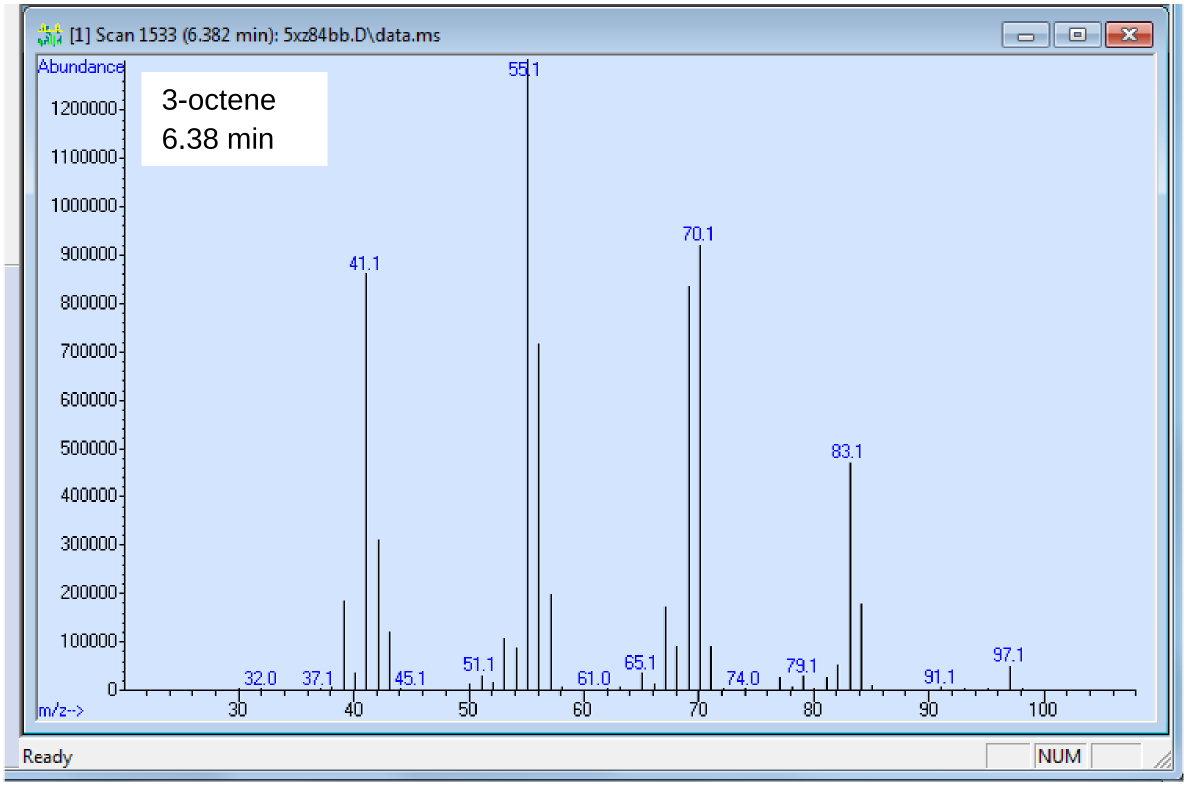


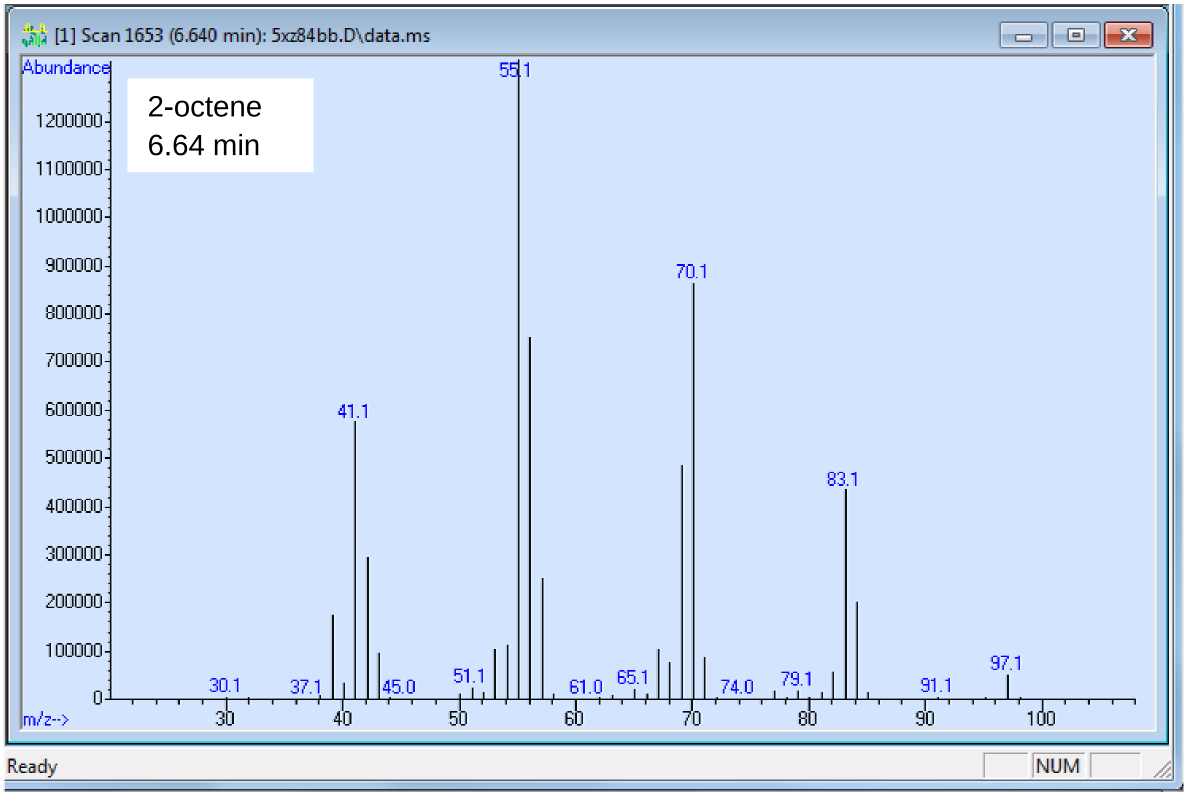

OH
3
5 mol % $H_4SiW_{12}O_{40}$
5 mol % $CuBr_2$
1.0 g NBu_4Br/0.10 mL *p*-xylene
24 h, 125 ºC
5
+
4
+
3
+ 2 additional octene isomers

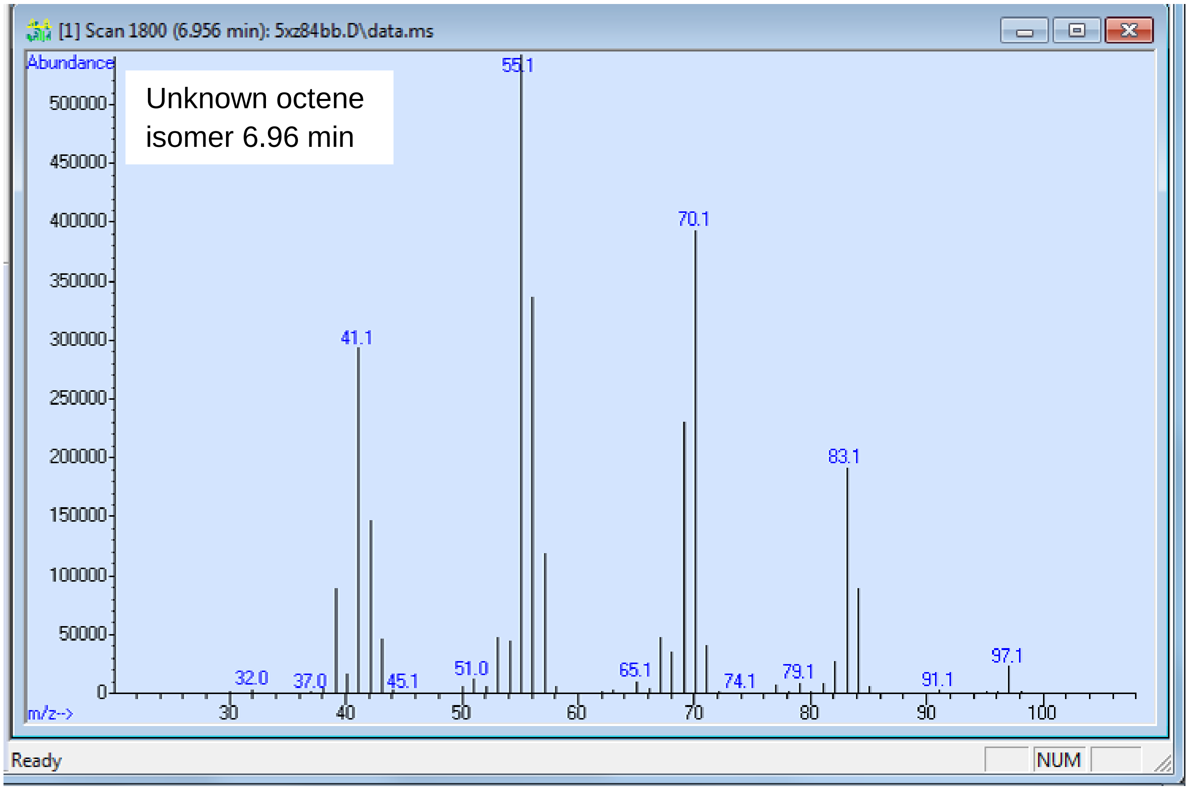

[2] TIC: 5xz83cc.D\data.ms
Abundance
2e+07
1.8e+07
1.6e+07
1.4e+07
1.2e+07
1e+07
8000000
6000000
4000000
2000000
Time-->
5.00
6.00
7.00
8.00
9.00
10.00
11.00
3-octene
6.38 min
Additional octene
isomers 6.25 / 6.96 min
p-xylene
9.49 min
2-octene
6.64 min
1-octene
6.04 min


[1] Scan 1374 (6.041 min): 5xz84bb.D\data.ms
Abundance
1-octene
6.04 min
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
m/z-->
30
40
50
60
70
80
90
100
32.0
39.0
43.1
51.0
55.1
65.1
70.1
77.0
83.1
91.1
97.1

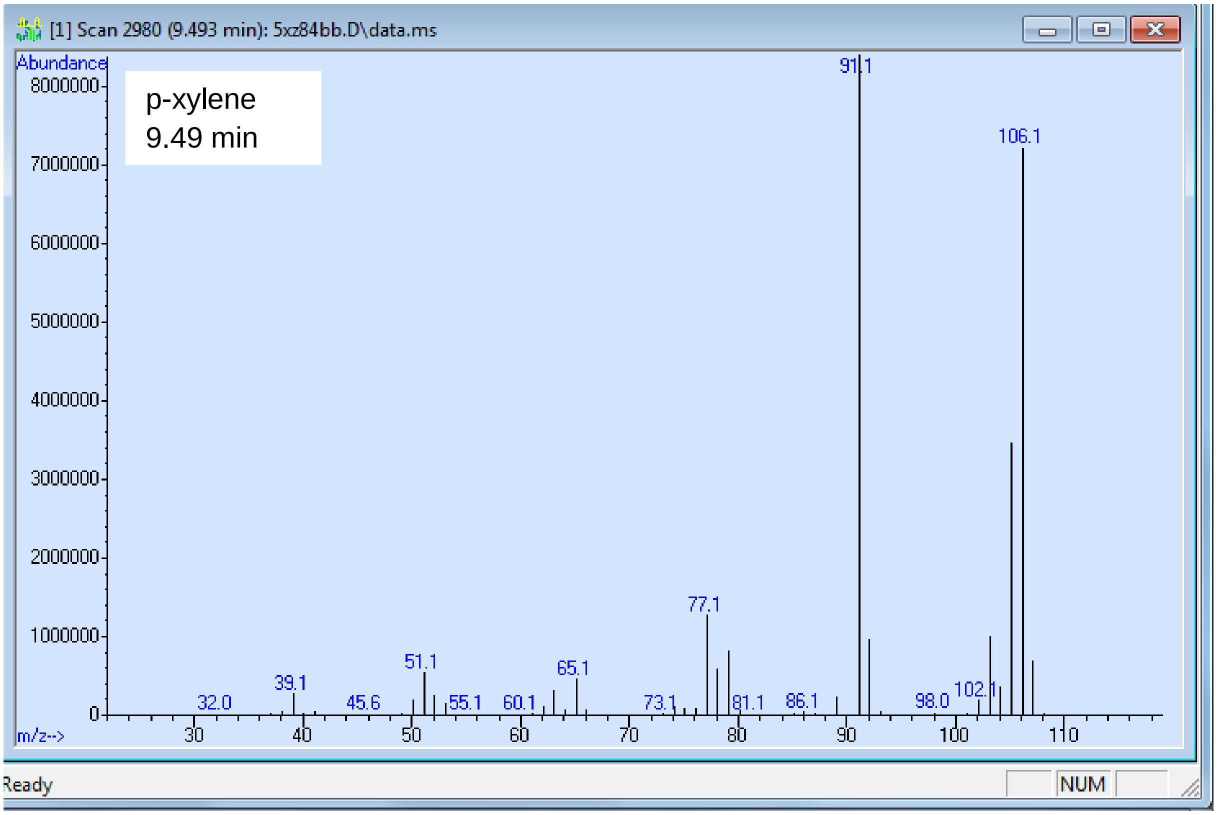

[1] Scan 1473 (6.253 min): 5xz84bb.D\data.ms
Abundance
Unknown octene
isomer 6.25 min
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
m/z-->
30
40
50
60
70
80
90
100
32.0
37.0
41.1
45.0
51.1
55.1
61.0
65.1
70.1
74.0
79.1
83.1
91.1
97.1
Ready
NUM


[1] Scan 1533 (6.382 min): 5xz84bb.D\data.ms
3-octene
6.38 min
Abundance
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
m/z-->
30
40
50
60
70
80
90
100
55.1
70.1
41.1
83.1
32.0
37.1
45.1
51.1
61.0
65.1
74.0
79.1
91.1
97.1
Ready
NUM


[1] Scan 1653 (6.640 min): 5xz84bb.D\data.ms
2-octene
6.64 min
Abundance
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
m/z-->
30
40
50
60
70
80
90
100
55.1
70.1
41.1
83.1
30.1
37.1
45.0
51.1
61.0
65.1
74.0
79.1
91.1
97.1
Ready
NUM


[1] Scan 1800 (6.956 min): 5xz84bb.D\data.ms

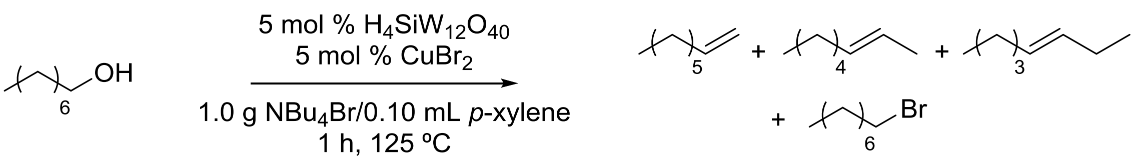
Unknown octene isomer 6.96 min

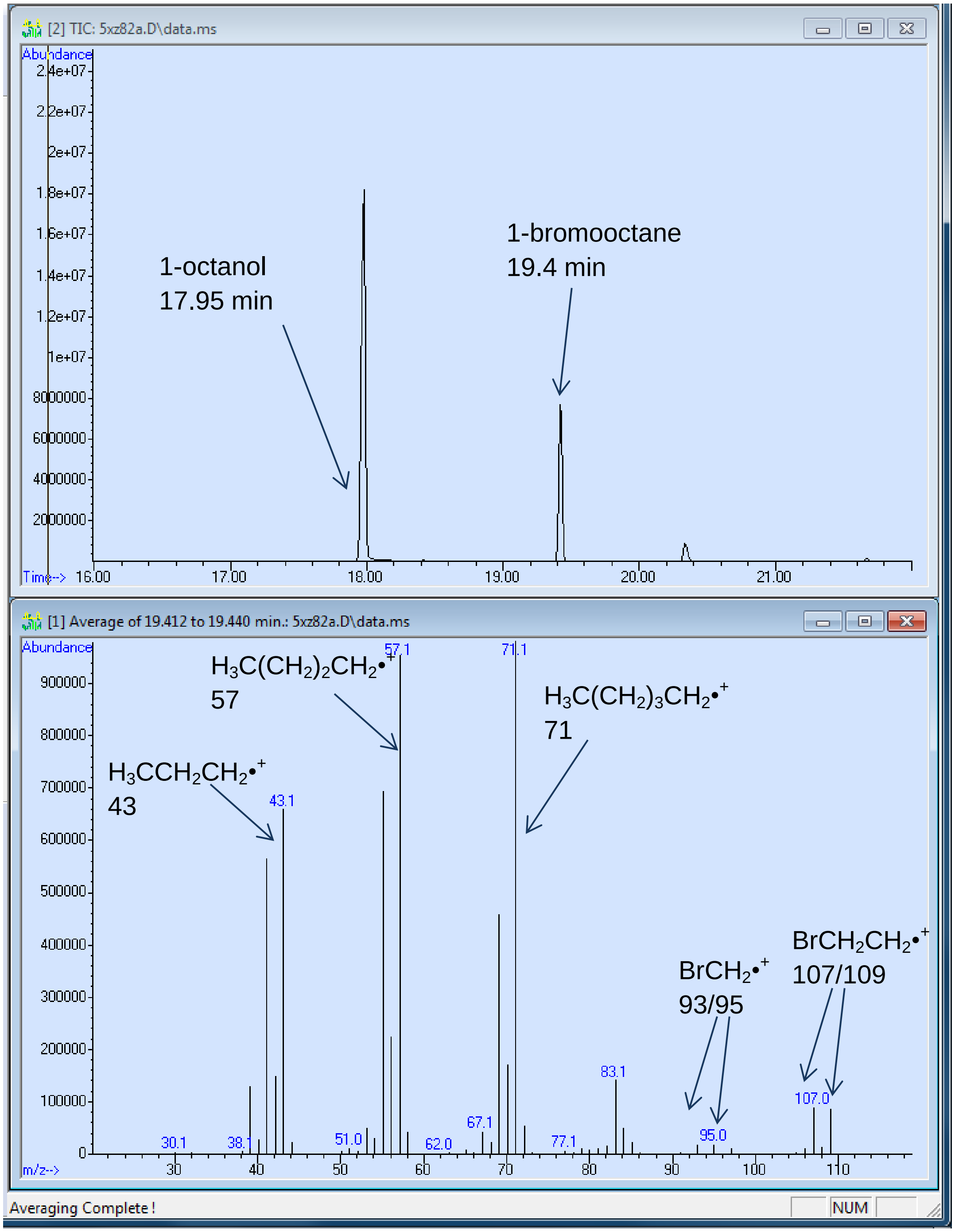

[1] Scan 2980 (9.493 min): 5xz84bb.D\data.ms

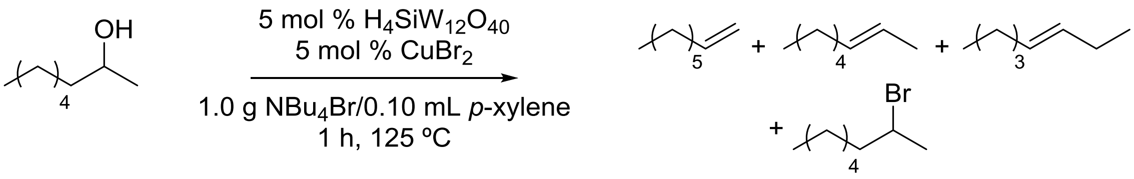
p-xylene
9.49 min

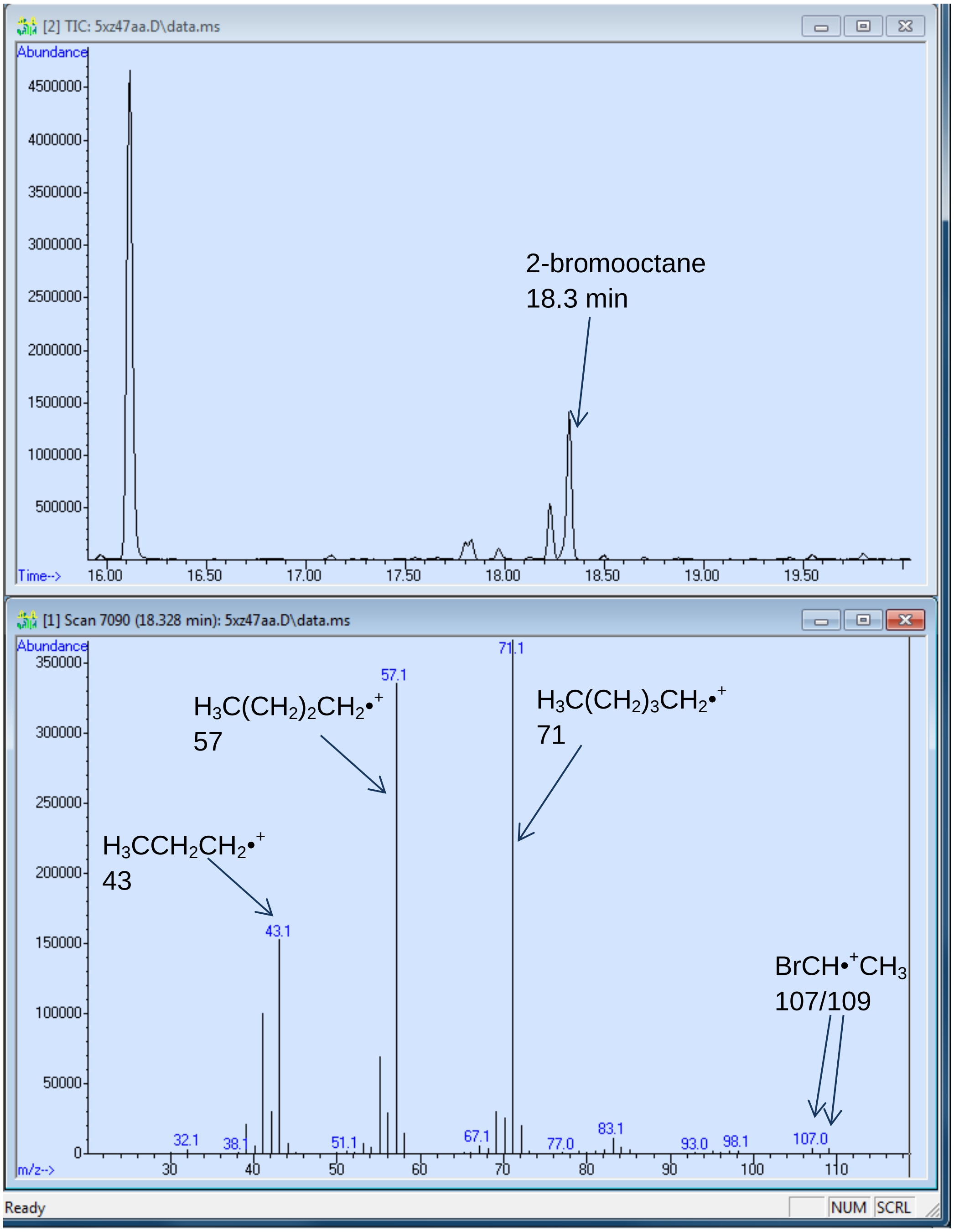
Detection of Brominated Intermediates

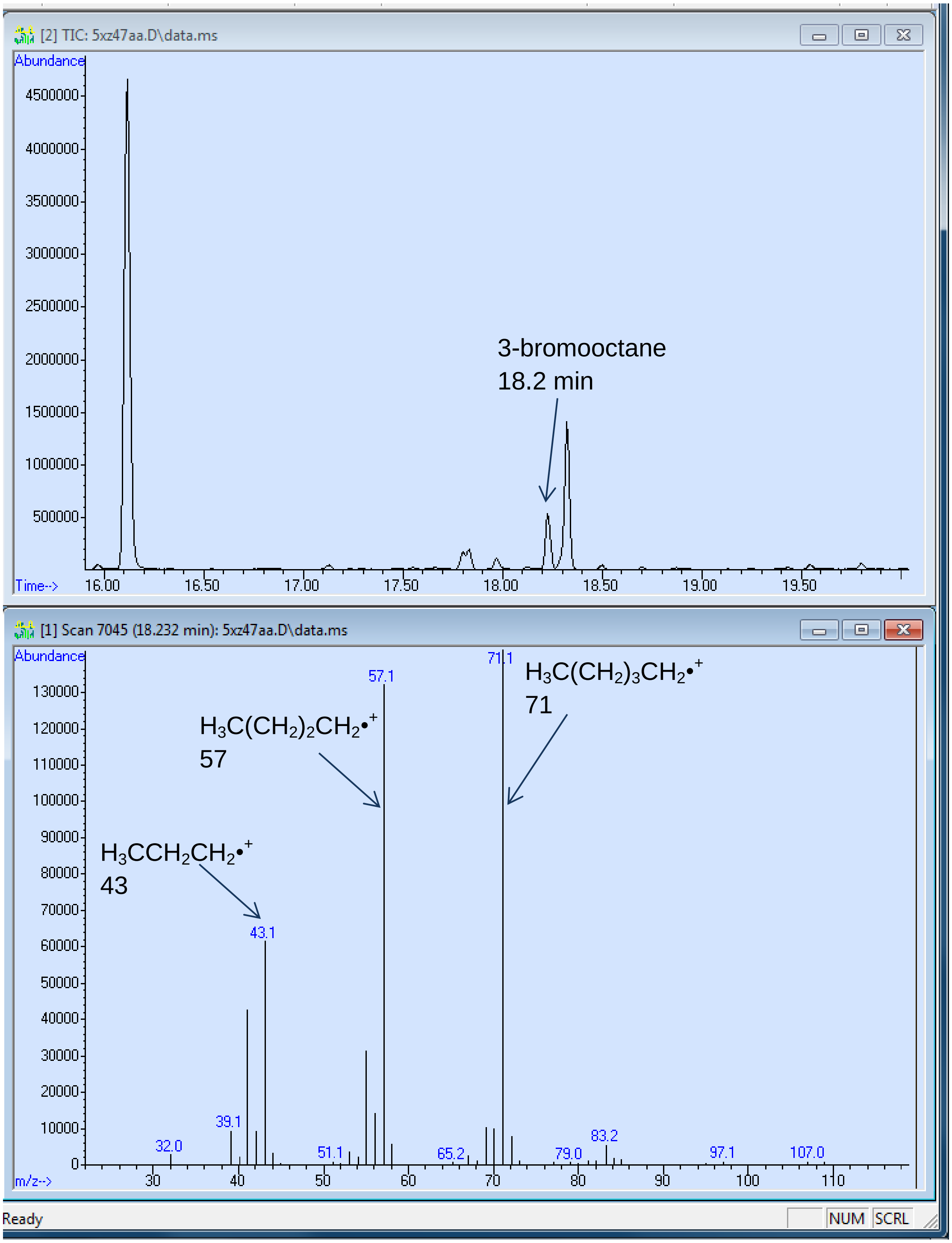
In analogy to General Procedure B, preactivated $H_4SiW_{12}O_{40}$ (91.5 mg, 31.8 µmol, 5.0 mol %), $CuBr_2$ (7.1 mg, 32 µmol, 5.0 mol %), NBu_4Br (1.00 g, 3.10 mmol, 4.88 equiv), *para*-xylene (0.10 mL; dried over 4Å MS before use), and alcohol (635 µmol, 1.00 equiv) were reacted at 125 °C for 1 h. Workup was performed as described in General Procedure B; analysis of the resulting mixture was performed by GCMS (see Figures below).

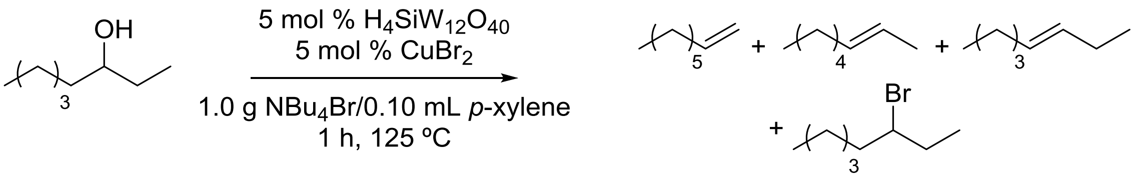

OH
6
5 mol % $H_4SiW_{12}O_{40}$
5 mol % $CuBr_2$
1.0 g NBu_4Br/0.10 mL *p*-xylene
1 h, 125 ºC
5
+
4
+
3
+
Br
6

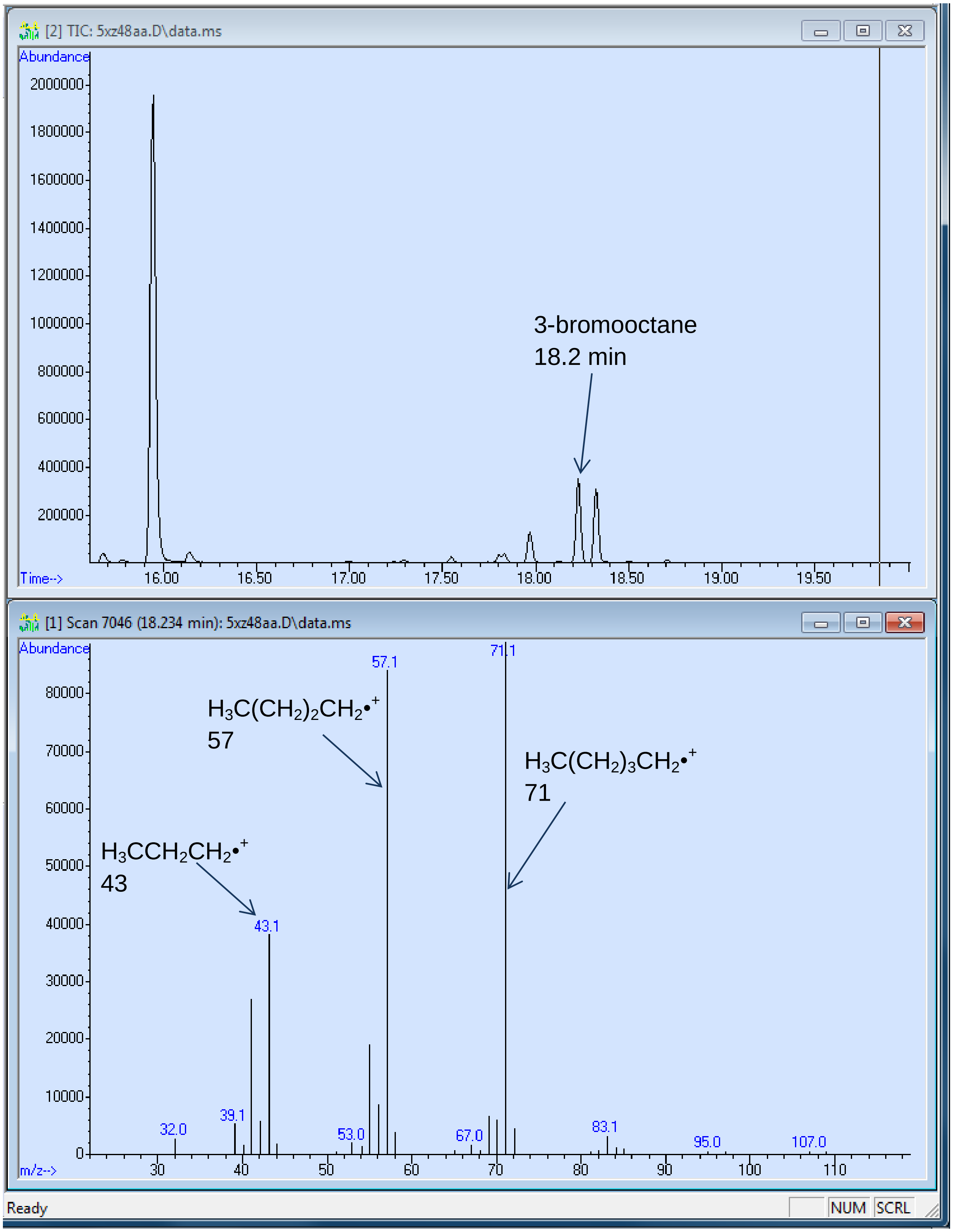

[2] TIC: 5xz82a.D\data.ms
Abundance
2.4e+07
2.2e+07
2e+07
1.8e+07
1.6e+07
1.4e+07
1.2e+07
1e+07
8000000
6000000
4000000
2000000
Time-->
16.00
17.00
18.00
19.00
20.00
21.00
1-octanol
17.95 min
1-bromooctane
19.4 min
[1] Average of 19.412 to 19.440 min.: 5xz82a.D\data.ms
Abundance
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
m/z-->
30
40
50
60
70
80
90
100
110
30.1
38.1
43.1
51.0
57.1
62.0
67.1
71.1
77.1
83.1
95.0
107.0
$H_3CCH_2CH_2•^+$
43
$H_3C(CH_2)_2CH_2•^+$
57
$H_3C(CH_2)_3CH_2•^+$
71
$BrCH_2•^+$
93/95
$BrCH_2CH_2•^+$
107/109
Averaging Complete !
NUM

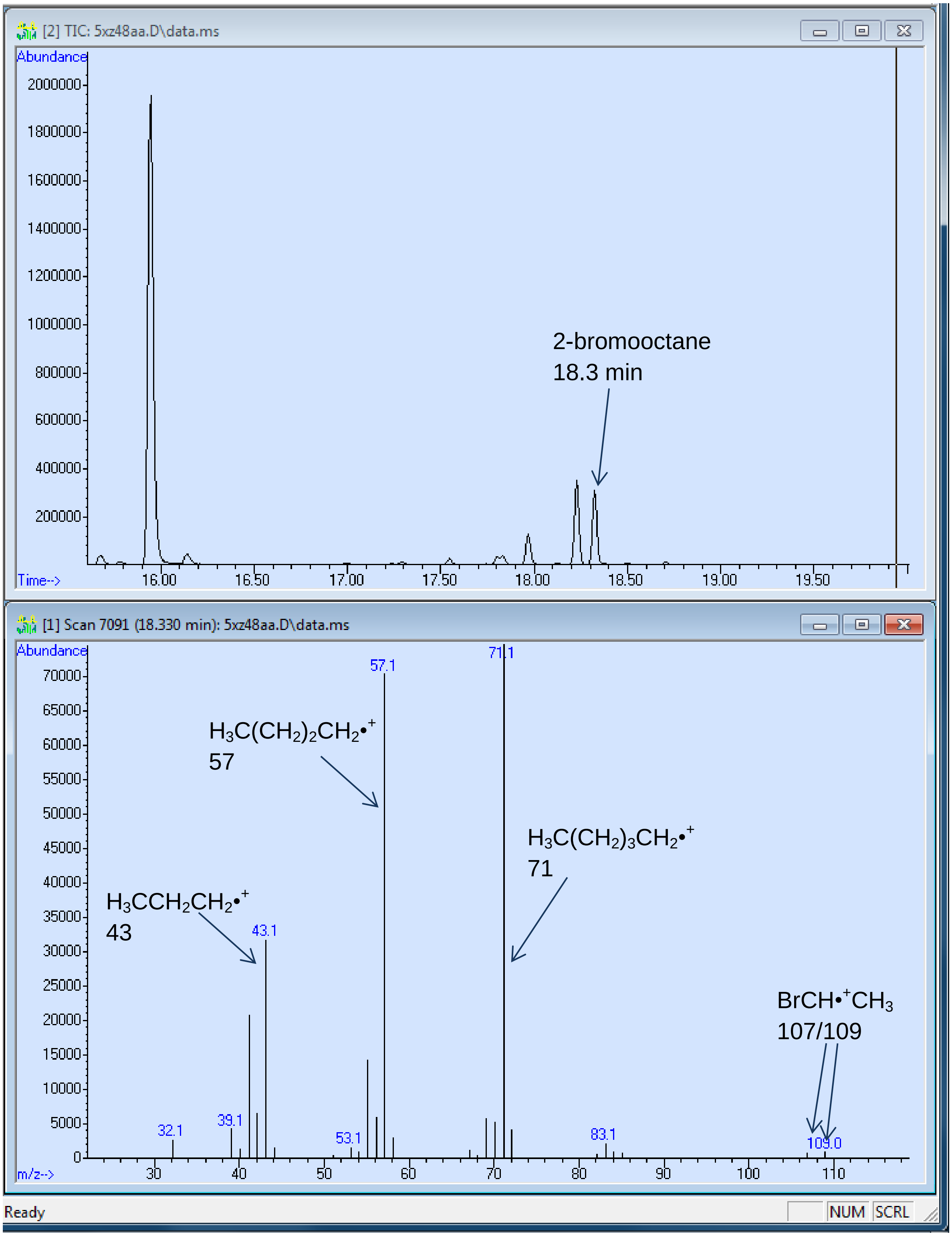

OH
4
5 mol % $H_4SiW_{12}O_{40}$
5 mol % $CuBr_2$
1.0 g NBu_4Br/0.10 mL *p*-xylene
1 h, 125 ºC
5
+
4
+
3
Br
+
4

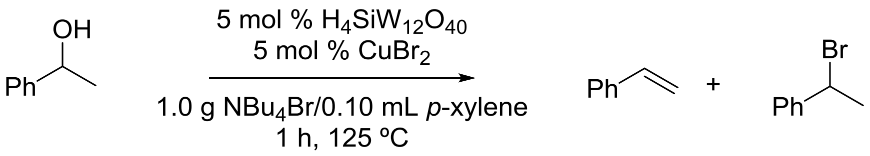

[2] TIC: 5xz47aa.D\data.ms
Abundance
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
Time-->
16.00
16.50
17.00
17.50
18.00
18.50
19.00
19.50
2-bromooctane
18.3 min
[1] Scan 7090 (18.328 min): 5xz47aa.D\data.ms
Abundance
350000
300000
250000
200000
150000
100000
50000
0
m/z-->
30
40
50
60
70
80
90
100
110
32.1
38.1
43.1
51.1
57.1
67.1
71.1
77.0
83.1
93.0
98.1
107.0
$H_3C(CH_2)_2CH_2\bullet^+$
57
$H_3C(CH_2)_3CH_2\bullet^+$
71
$H_3CCH_2CH_2\bullet^+$
43
$BrCH\bullet^+CH_3$
107/109
Ready
NUM
SCRL


[2] TIC: 5xz47aa.D\data.ms
Abundance
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
Time-->
16.00
16.50
17.00
17.50
18.00
18.50
19.00
19.50
3-bromooctane
18.2 min
[1] Scan 7045 (18.232 min): 5xz47aa.D\data.ms
Abundance
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
m/z-->
30
40
50
60
70
80
90
100
110
32.0
39.1
43.1
51.1
57.1
65.2
71.1
79.0
83.2
97.1
107.0
$H_3C(CH_2)_3CH_2\bullet^+$
71
$H_3C(CH_2)_2CH_2\bullet^+$
57
$H_3CCH_2CH_2\bullet^+$
43
Ready
NUM
SCRL

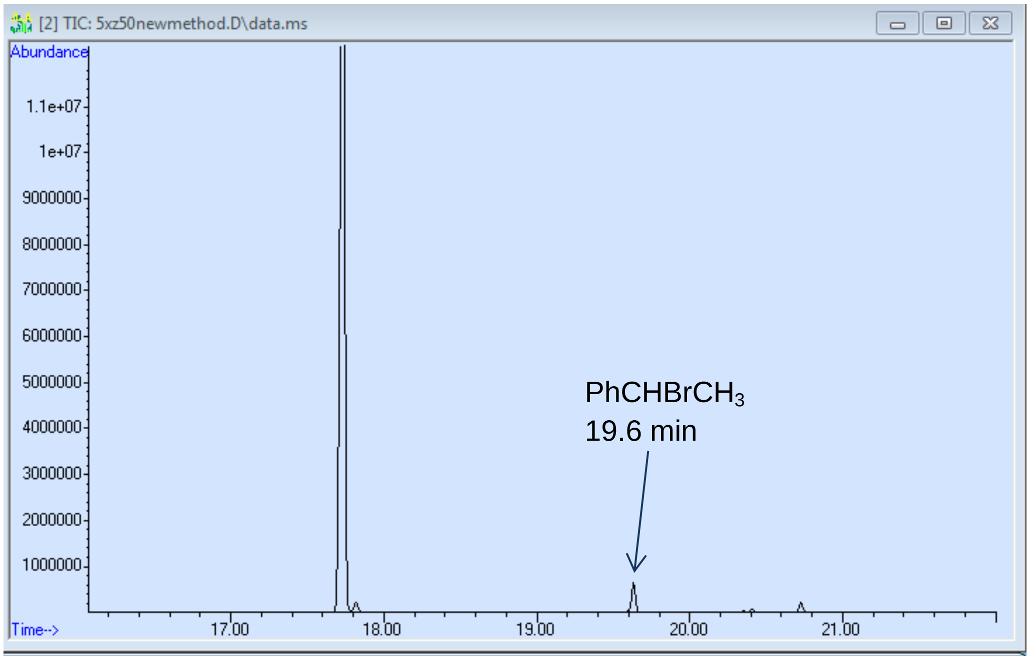

OH
3
5 mol % $H_4SiW_{12}O_{40}$
5 mol % $CuBr_2$
1.0 g NBu_4Br/0.10 mL *p*-xylene
1 h, 125 ºC
5
+
4
+
3
Br
+
3


[2] TIC: 5xz48aa.D\data.ms
Abundance
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
Time-->
16.00
16.50
17.00
17.50
18.00
18.50
19.00
19.50
3-bromooctane
18.2 min
[1] Scan 7046 (18.234 min): 5xz48aa.D\data.ms
Abundance
80000
70000
60000
50000
40000
30000
20000
10000
0
m/z-->
30
40
50
60
70
80
90
100
110
57.1
71.1
43.1
39.1
32.0
53.0
67.0
83.1
95.0
107.0
$H_3C(CH_2)_2CH_2•^+$
57
$H_3C(CH_2)_3CH_2•^+$
71
$H_3CCH_2CH_2•^+$
43
Ready
NUM
SCRL

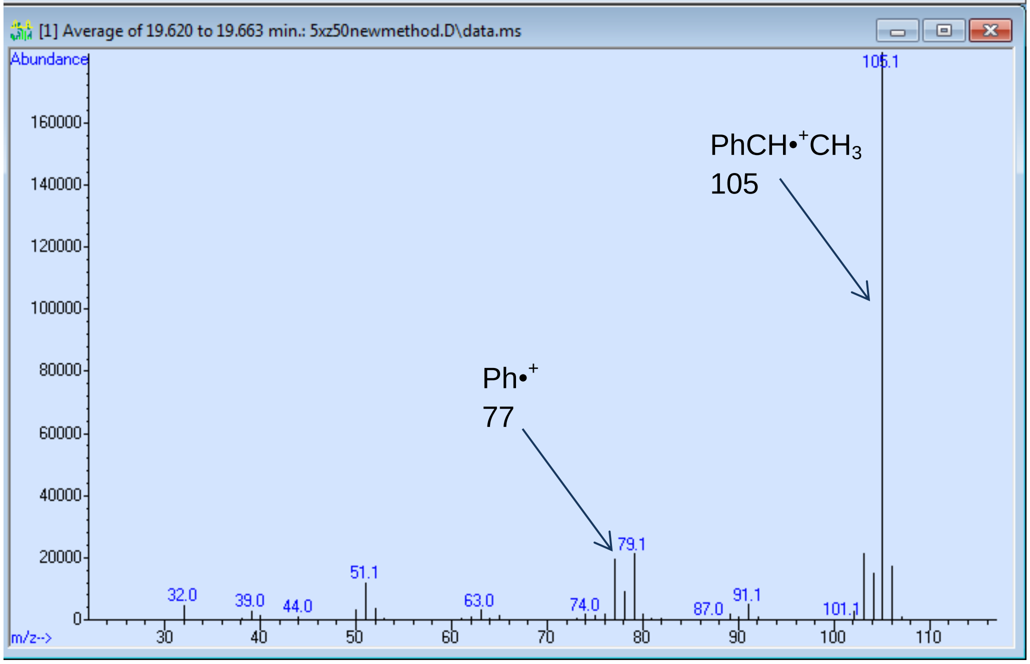

[2] TIC: 5xz48aa.D\data.ms
Abundance
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
Time-->
16.00
16.50
17.00
17.50
18.00
18.50
19.00
19.50
2-bromooctane
18.3 min
[1] Scan 7091 (18.330 min): 5xz48aa.D\data.ms
Abundance
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
m/z-->
30
40
50
60
70
80
90
100
110
57.1
71.1
43.1
39.1
32.1
53.1
83.1
109.0
$H_3C(CH_2)_2CH_2•^+$
57
$H_3C(CH_2)_3CH_2•^+$
71
$H_3CCH_2CH_2•^+$
43
$BrCH•^+CH_3$
107/109
Ready
NUM
SCRL



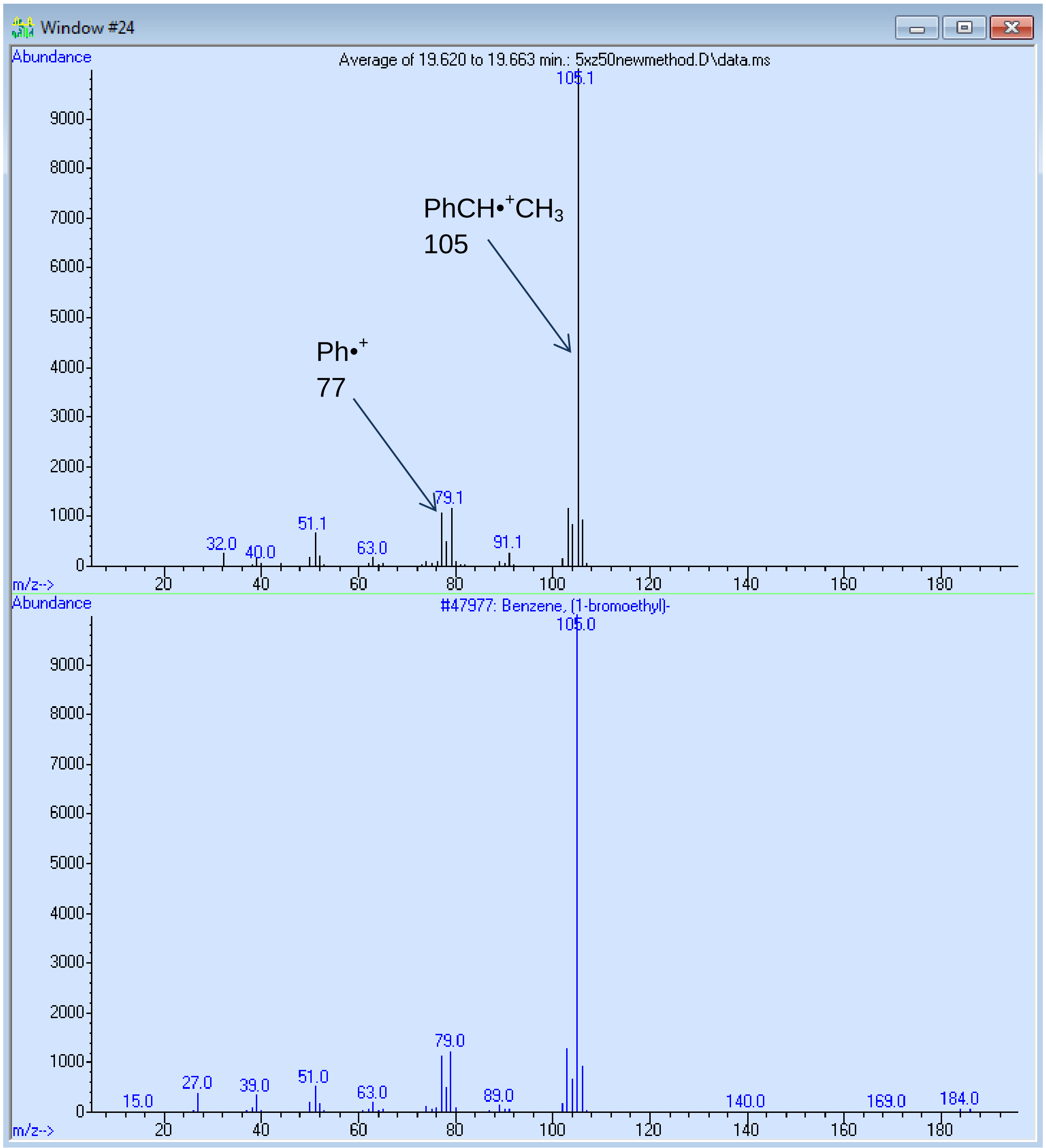
OH
Ph
5 mol % $H_4SiW_{12}O_{40}$
5 mol % $CuBr_2$
1.0 g NBu_4Br/0.10 mL *p*-xylene
1 h, 125 ºC
Ph
+
Br
Ph

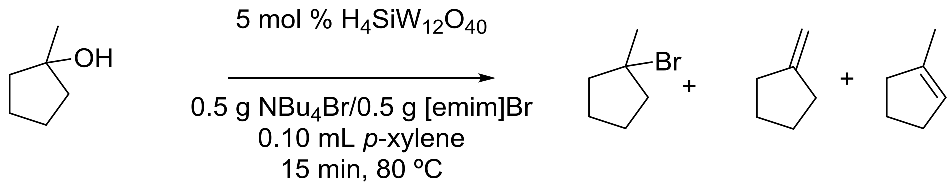


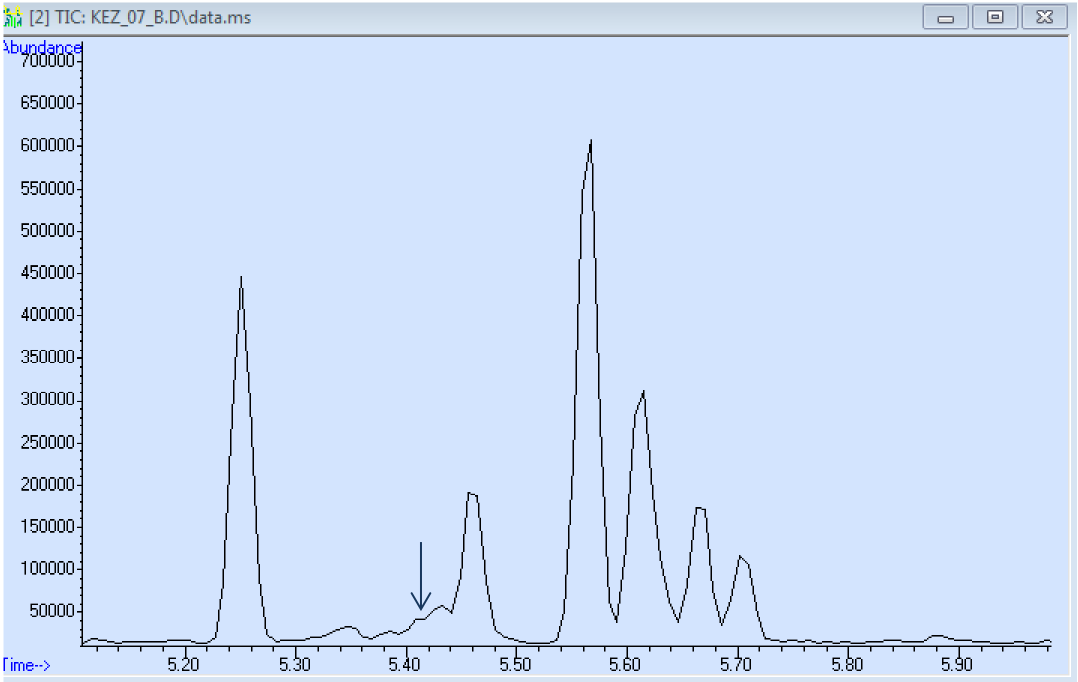
[2] TIC: 5xz50newmethod.D\data.ms
Abundance
1.1e+07
1e+07
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
Time-->
17.00
18.00
19.00
20.00
21.00
$PhCHBrCH_3$
19.6 min

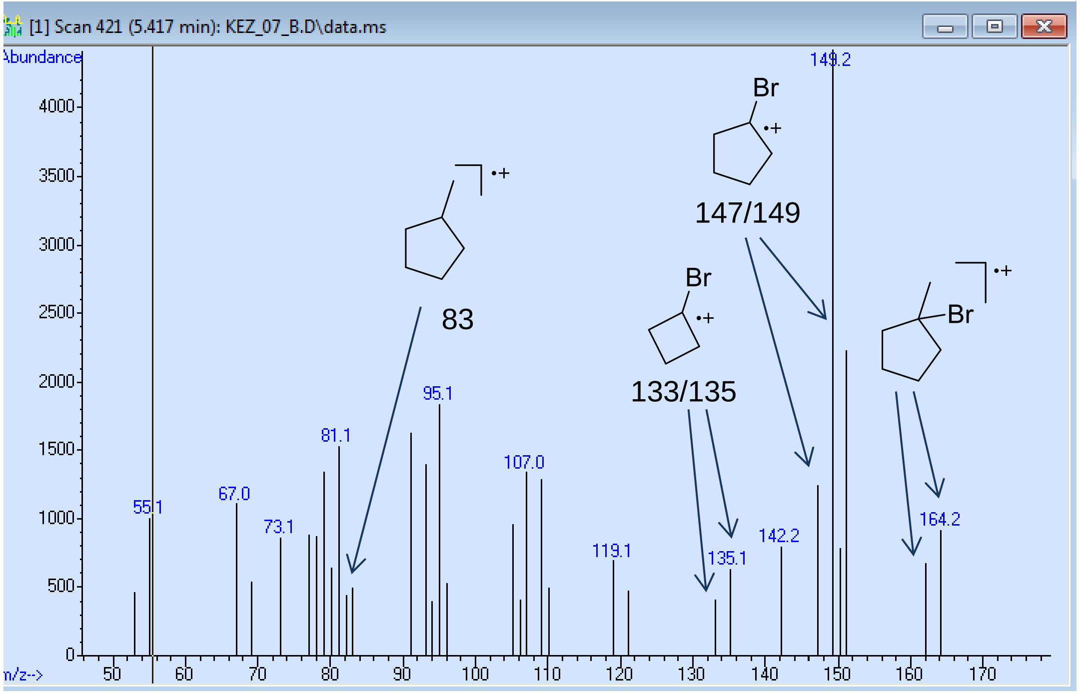


[1] Average of 19.620 to 19.663 min.: 5xz50newmethod.D\data.ms
Abundance
160000
140000
120000
100000
80000
60000
40000
20000
0
m/z-->
30
40
50
60
70
80
90
100
110
105.1
$PhCH•^+CH_3$
105
$Ph•^+$
77
79.1
51.1
32.0
39.0
44.0
63.0
74.0
87.0
91.1
101.1


Window #24
Abundance
Average of 19.620 to 19.663 min.: 5xz50newmethod.D\data.ms
105.1
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
$PhCH^{\bullet+}CH_3$
105
$Ph^{\bullet+}$
77
79.1
51.1
32.0
40.0
63.0
91.1
m/z-->
20
40
60
80
100
120
140
160
180
Abundance
#47977: Benzene, (1-bromoethyl)-
105.0
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
79.0
51.0
27.0
39.0
15.0
63.0
89.0
140.0
169.0
184.0
m/z-->
20
40
60
80
100
120
140
160
180

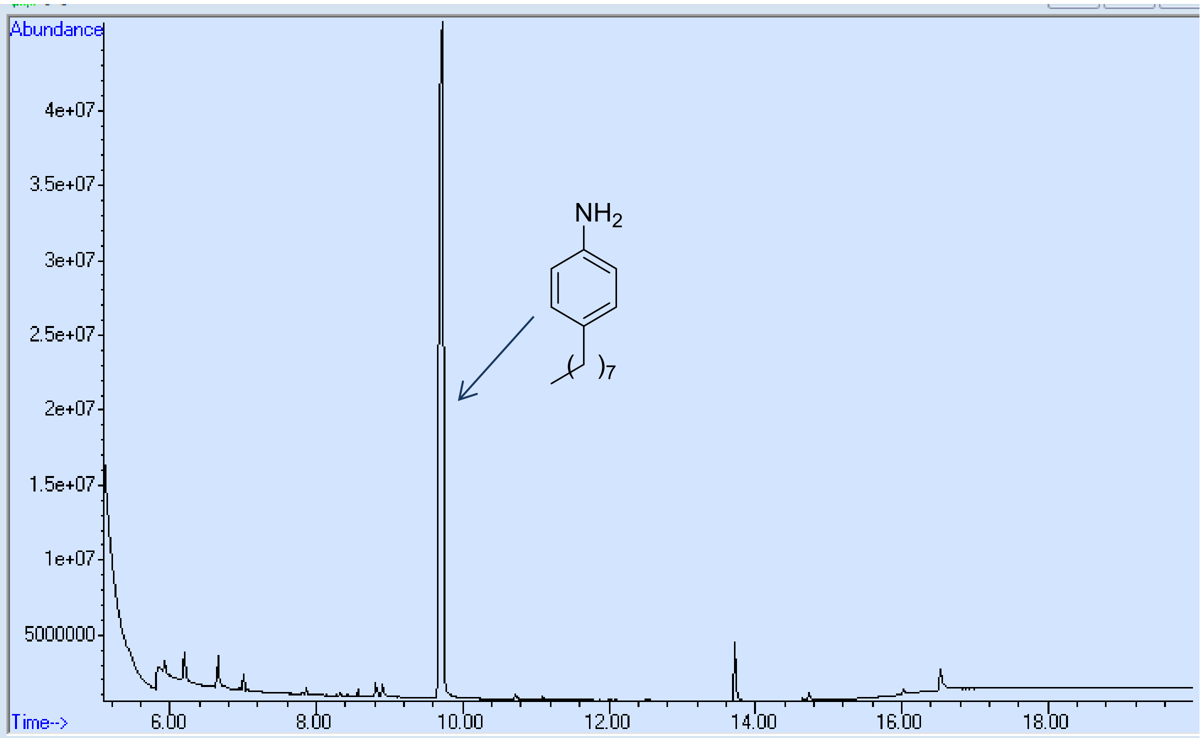

OH
5 mol % $H_4SiW_{12}O_{40}$
0.5 g NBu_4Br/0.5 g [emim]Br
0.10 mL *p*-xylene
15 min, 80 ºC
Br
+
+

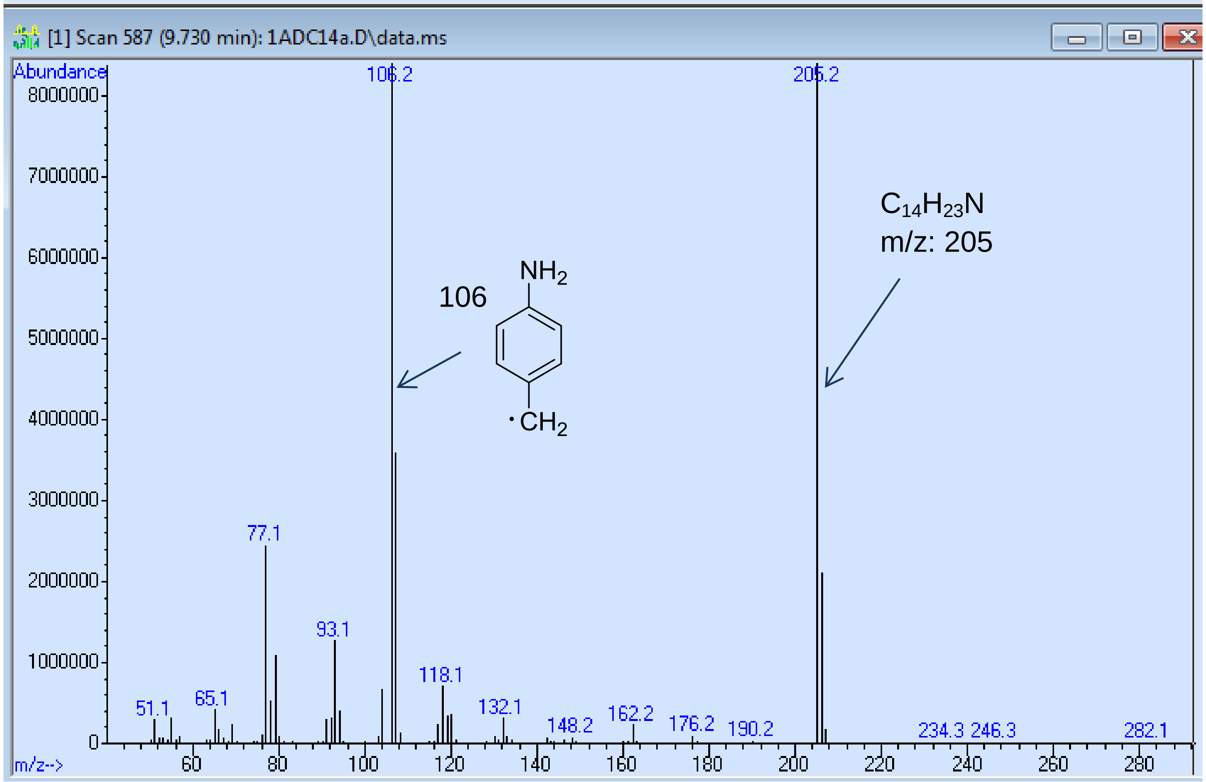

[2] TIC: KEZ_07_B.D\data.ms
Abundance
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
Time-->
5.20
5.30
5.40
5.50
5.60
5.70
5.80
5.90


[1] Scan 421 (5.417 min): KEZ_07_B.D\data.ms
Abundance
4000
3500
3000
2500
2000
1500
1000
500
0
m/z-->
50
60
70
80
90
100
110
120
130
140
150
160
170
55.1
67.0
73.1
81.1
95.1
107.0
119.1
135.1
142.2
149.2
164.2
•+
83
Br
•+
133/135
Br
•+
147/149
Br
•+

Friedel-Crafts Reaction under C-O Activation Conditions

In analogy to General Procedure B, preactivated $H_4SiW_{12}O_{40}$ (91.5 mg, 31.8 µmol, 5.0 mol %), NBu_4Br (1.0 g, 3.1 mmol, 4.9 equiv), aniline (3.0 mL, 3.1 g, 33 mmol, 52 equiv), *para*-xylene (0.10 mL; dried over 4Å MS before use), and 1-bromooctane (110 µL, 123 mg, 635 µmol, 1.00 equiv) were reacted at 125 °C for 1 h. The reaction mixture was then allowed to cool to room temperature. PhOAc (100 µL, 107 mg, 788 µmol) as internal GC standard, DI H_2O (3 mL), and saturated organic K_2CO_3 solution (1 mL) were added. The resulting mixture was extracted with Et_2O (5 mL). The combined organic phases were filtered through celite and the yield of 4-octylaniline was determined by calibrated GC analysis (87 ± 1%). Isomeric purity and the identify of the product was established by GCMS (see below) and by comparison of retention times and fragmentation patterns with commercially available, identical 4-octyl aniline.


Abundance
4e+07
3.5e+07
3e+07
2.5e+07
2e+07
1.5e+07
1e+07
5000000
Time-->
6.00
8.00
10.00
12.00
14.00
16.00
18.00
NH2
)7

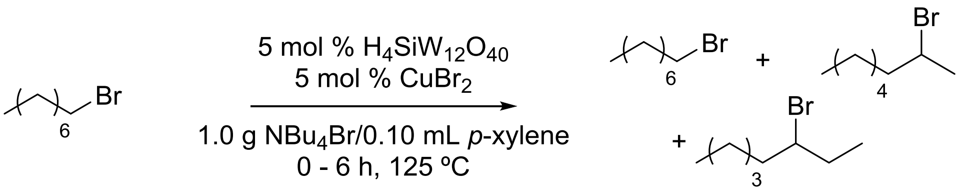

[1] Scan 587 (9.730 min): 1ADC14a.D\data.ms
Abundance
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
m/z-->
106.2
205.2
77.1
93.1
118.1
132.1
148.2
162.2
176.2
190.2
234.3
246.3
282.1
51.1
65.1
60
80
100
120
140
160
180
200
220
240
260
280
106
NH2
•CH2
C14H23N
m/z: 205

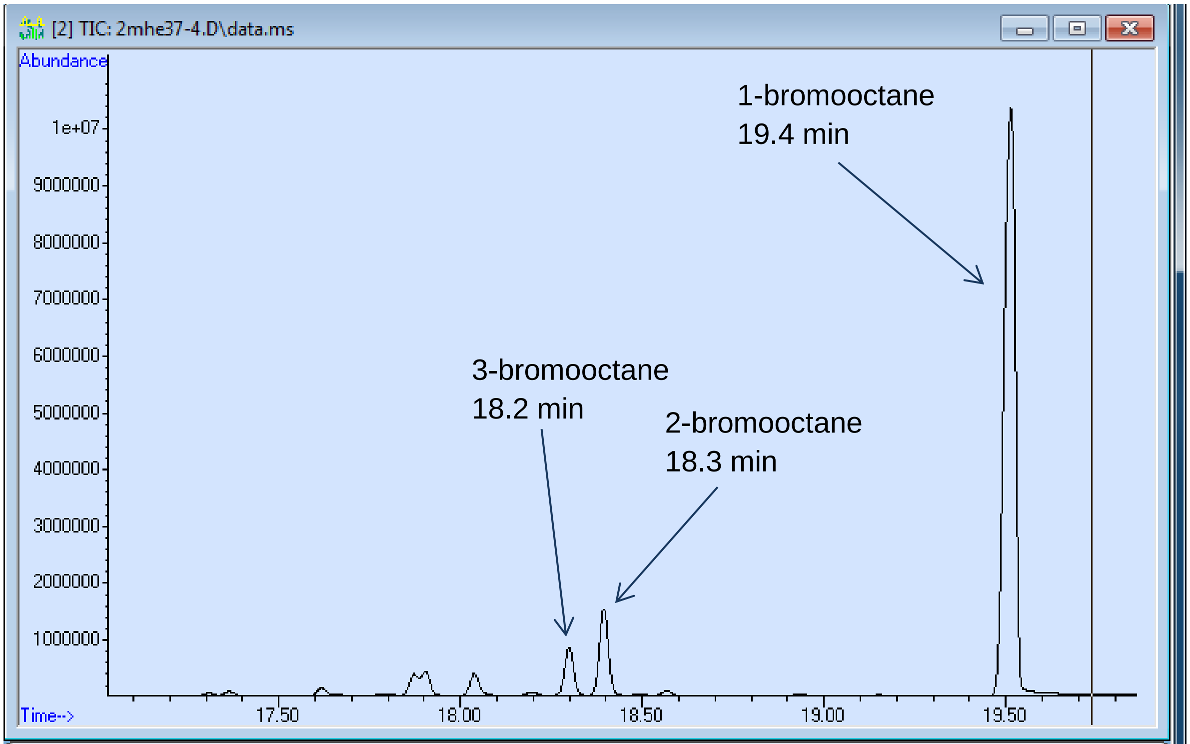
Tandem C-O Activation/C-C Bond Formation

Preactivated $H_4SiW_{12}O_{40}$ (183 mg, 63.5 µmol, 10.0 mol %), NBu_4Br (1.00 g, 3.01 mmol, 4.74 equiv.), [emim]Br (1.00 g, 5.23 mmol, 8.24 equiv.), PhCl (0.10 mL; dried over 4Å MS before use), and 1-octanol (0.10 mL, 0.083 g, 635 µmol, 1.00 equiv.) were reacted at 110 °C for 4 h. The vial was taken off the hotplate and after cooling to room temperature, aniline (3.0 mL, 3.06 g, 32.9 mmol, 52 equiv.) was added. The reaction mixture was then heated to 110 °C for 16 h. The reaction mixture was then allowed to cool to room temperature. DI H_2O (5 mL), saturated K_2CO_3 solution (1 mL), and PhOAc (100 µL, 0.11 g, 0.81 mmol) as internal GC standard were added. The resulting mixture was extracted with Et_2O (5 mL). The combined organic phases were filtered through celite and the yield of 4-octylaniline was determined by calibrated GC analysis (35%).

Reaction of 1-Bromooctane – Observation of Isomerized Bromooctanes

In analogy to General Procedure B, preactivated $H_4SiW_{12}O_{40}$ (91.5 mg, 31.8 µmol, 5.0 mol %), $CuBr_2$ (7.1 mg, 32 µmol, 5.0 mol %), NBu_4Br (1.00 g, 3.10 mmol, 4.88 equiv), *para*-xylene (0.10 mL; dried over 4Å MS before use), and 1-bromooctane (635 µmol, 1.00 equiv) were reacted at 125 °C. Samples were taken after reaction times of 10 min, 30 min, 1.5 h, 3 h, and 6 h. For sampling, the reaction mixture was removed from the hotplate and the vial was half submerged into a water bath at room temperature. After 5 min, the vial was opened and a glass pipette was used to sample some of the liquid on the vial walls as well as sample the slurry on the bottom of the vial. The resulting slurry was suspended in EtOAc (10 mL). After sampling, the vial was resealed with a Teflon-lined vial cap and placed on the vial plate. Analysis of the resulting mixtures was performed by GCMS, showing an increasing amount of isomerized bromooctanes in the reaction mixture with increasing reaction time. The figures below show the GCMS data obtained after 3 h reaction time.

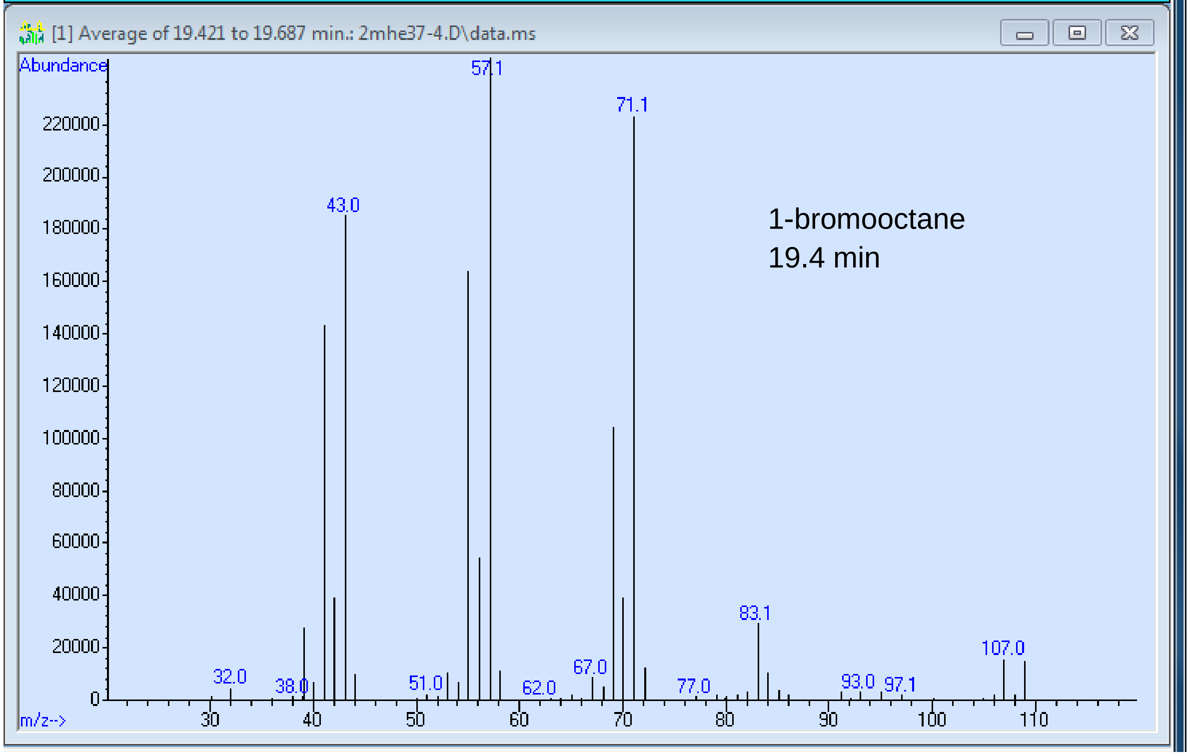



[2] TIC: 2mhe37-4.D\data.ms

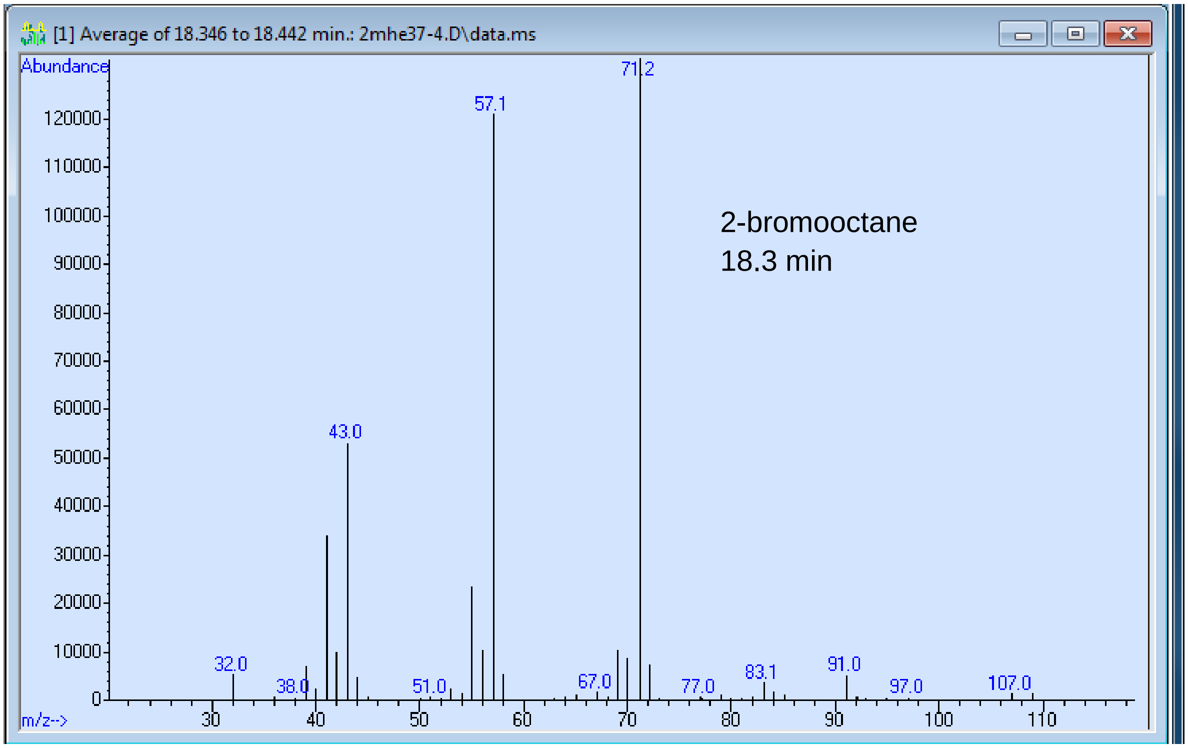
1-bromooctane
19.4 min

3-bromooctane
18.2 min

2-bromooctane
18.3 min

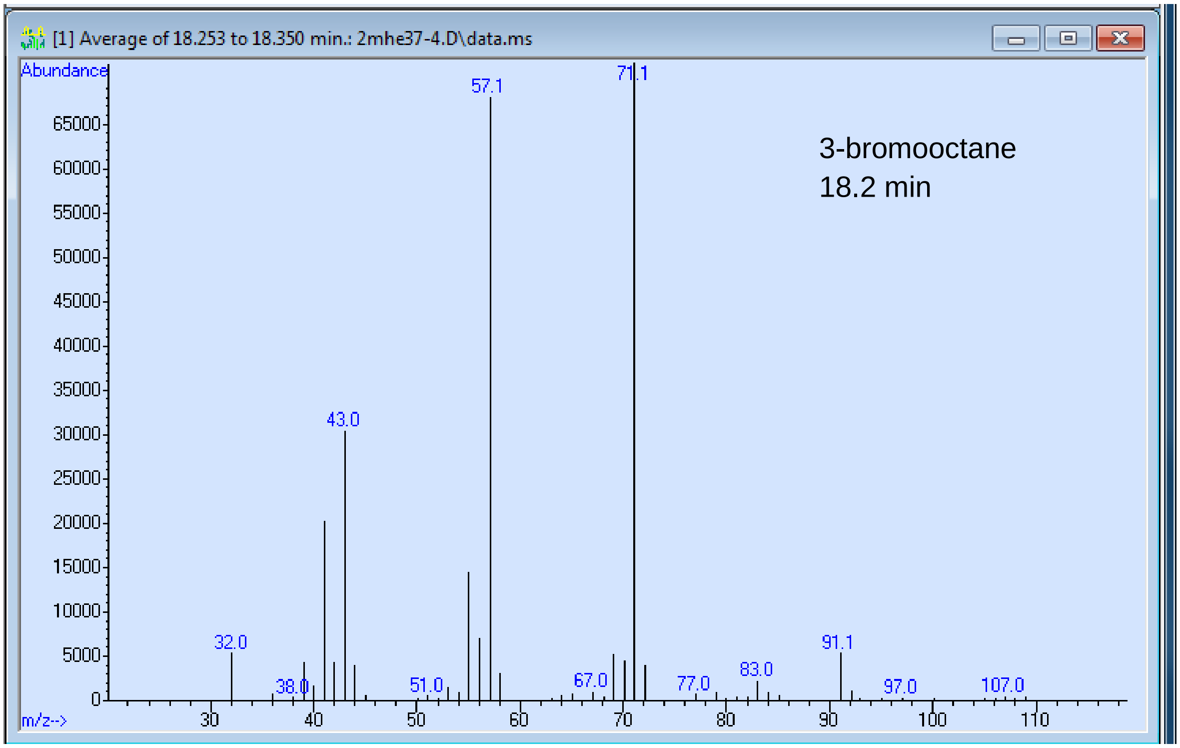

[1] Average of 19.421 to 19.687 min.: 2mhe37-4.D\data.ms

1-bromooctane
19.4 min



[1] Average of 18.346 to 18.442 min.: 2mhe37-4.D\data.ms

2-bromooctane
18.3 min



[1] Average of 18.253 to 18.350 min.: 2mhe37-4.D\data.ms

3-bromooctane
18.2 min

Reaction of 1-Octene in Dehydration Reaction of 1-Decanol

In analogy to General Procedure B, preactivated $H_4SiW_{12}O_{40}$ (91.5 mg, 31.8 µmol, 5.0 mol %), $CuBr_2$ (7.1 mg, 32 µmol, 5.0 mol %), NBu_4Br (1.00 g, 3.10 mmol, 4.88 equiv), *para*-xylene (0.10 mL; dried over 4Å MS before use), 1-decanol (635 µmol, 1.00 equiv), and 1-octene (635 µmol, 1.00 equiv) were reacted at 125 °C for 48 h. Workup and analysis were performed as described in General Procedure B. No dioctylether was observed. The yields of olefins were determined by calibrated GC analysis, using PhOAc as internal standard, to be as follows: 65% 1-octene; 12% 2-octene; 2% 3-octene; 30% 1-decene; 4% 2-decene; 1% 3-decene.