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Supplementary Material

Catalyst screening for dehydration of primary alcohols from renewable feedstocks under formation of alkenes at energy-saving mild reaction conditions

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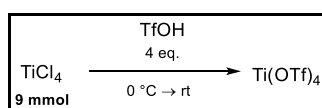
Experimental reagents

Chemicals were commercially bought without any further purification. Reactions were performed under atmospheric pressure or reduced pressure if noted.

Substrates: 1-Hexanol (Alfa Aesar, 99 %), 1-heptanol (THERMO SCIENTIFIC, 99 %), 1-octanol (THERMO SCIENTIFIC, 99 %), 1-nonanol (TCI, > 99 %), 1-decanol (ROTH, > 99 %), 1-undecanol (TCI, > 99 %), 1-dodecanol (TCI, > 99 %) and di-*n*-hexyl ether (TCI, >98 %) were purchased from commercial sources.

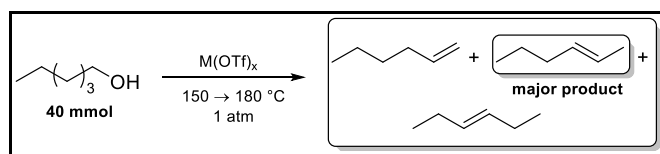
Catalysts: Yb(OTf)₃ (BLDPHARM, 99.3 %), Y(OTf)₃ (SIMA ALDRICH, 98 %), La(OTf)₃ (ALFA AESAR, 99 %), Dy(OTf)₃ (ALFA AESAR, 98 %), Er(OTf)₃ (SIGMA ALDRICH, 98 %), Mn(OTf)₃ (SIGMA ALDRICH, 95 %), Sc(OTf)₃ (BLDPHARM, 99 %), AgOTf (SIGMA ALDRICH, > 99 %), Cu(OTf)₂ (TCI, > 98 %), Al(OTf)₃ (SIGMA ALDRICH, 99.9 %), Fe(OTf)₃ (ALFA AESAR, 90 %), Bi(OTf)₃ (STREM, 98 %), Hf(OTf)₄ (THERMO SCIENTIFIC, 98 %), NaOTf (SIGMA ALDRICH, 98 %) and KOTf (SIGMA ALDRICH, 98 %) were also purchased. Ti(OTf)₄ was produced from TiCl₄ (SIGMA ALDRICH, > 97 %) and TfOH (FLUOROCHEM, 99 %) accordingly to literature.¹

Synthesis of Ti(OTf)₄



The synthesis of Ti(OTf)₄ was carried out under standard SCHLENK conditions. A 25 mL SCHLENK flask and dropping funnel were flamed out. The flask was connected to three wash bottles containing CaCl₂, nothing or 1 M NaOH. In the SCHLENK flask triflic acid (3.3 mL, 36 mmol, 4 eq.) was put. Under constant Ar-flow and ice bath cooling TiCl₄ (1 mL, 9 mmol, 1 eq.) was dripped to triflic acid for 10 min. Afterwards, the reaction mixture was brought to rt and stirred for 3 h. The reaction was quenched by the adding of 10 mL dH₂O and allowed to stir for 1.5 h at rt. To remove water and unreacted substrates a distillation apparatus was used at a high vacuum and up to 80 °C. The temperature was slowly heated to avoid boiling delay. Furthermore, heating to 180 °C was done to crystallize the product. A light pinkish solid was formed. Ti(OTf)₄ was obtained with a yield of 70 %.

Dehydration using 2 mol% metal triflates at 180 °C oil bath temperature



1-hexanol (**1**) (5 mL, 40 mmol) was put together with a catalyst (2 mol%) in a 25 mL round flask and connected to a micro distillation bridge. After heating it for 1.5 hour at 150 °C the temperature was further heated to 180 °C. The reaction was done for 6 – 22 h. After the distillation was finished two phases were obtained. Through a separation of the organic phase from the water phase the crude yield was obtained. The crude yield was then determined and the hexene purity determined through $^1\text{H-NMR}$ spectras. In case of $\text{Sc}(\text{OTf})_3$ the ether was isolated by column chromatography with a yield of 83 %.

Table 1: Dehydration of 1-hexanol (**1**) by 2 mol% metal triflates.

| Metal triflate | Weight | Reaction time | Crude yield | Hexene purity | Ether yield |
|----------------|--------|---------------|-------------|---------------|-------------|
| Yb(III) | 496 mg | 22 h | 0 | - | - |
| Y(III) | 429 mg | 22 h | 0 | - | - |
| La(III) | 469 mg | 22 h | 0 | - | - |
| Dy(III) | 488 mg | 22 h | 0 | - | - |
| Er(III) | 492 mg | 22 h | 0 | - | - |
| Mn(II) | 283 mg | 22 h | 0 | - | - |
| Sc(III) | 394 mg | 22 h | - | - | 83 % |
| Ag(I) | 206 mg | 22 h | 67 | 94 % | - |
| Cu(II) | 288 mg | 22 h | 68 | 95 % | - |
| Al(III) | 380 mg | 12 h | 82 % | 97 % | - |
| Fe(III) | 403 mg | 12 h | 83 % | 86 % | - |
| Bi(III) | 525 mg | 6 h | 89 % | 92 % | - |
| Ti(IV) | 515 mg | 6 h | 78 % | 90 % | - |
| Hf(IV) | 621 mg | 6 h | 83 % | 90 % | - |
| KOTf(I) | 151 mg | 22 h | 0 | - | - |
| Na(I) | 140 mg | 22 h | 0 | - | - |

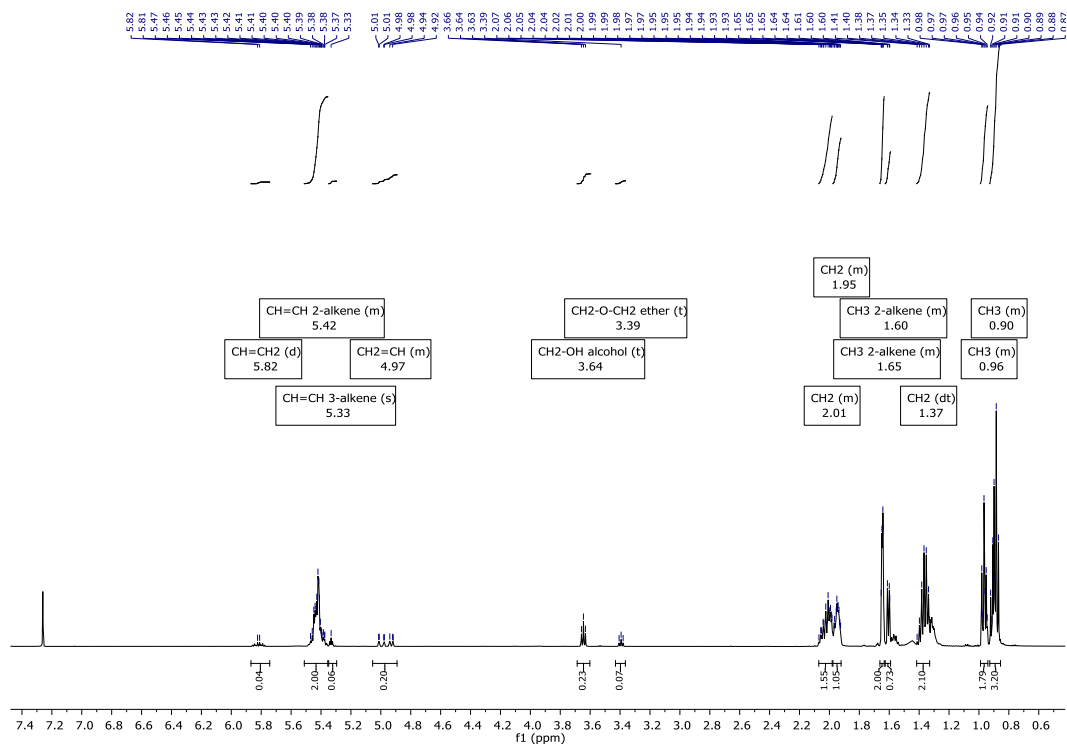


Figure 1: $^1\text{H-NMR}$ spectrum of the dehydration of 1-hexanol by $\text{Hf}(\text{OTf})_4$ in CDCl_3 .

1-hexene:

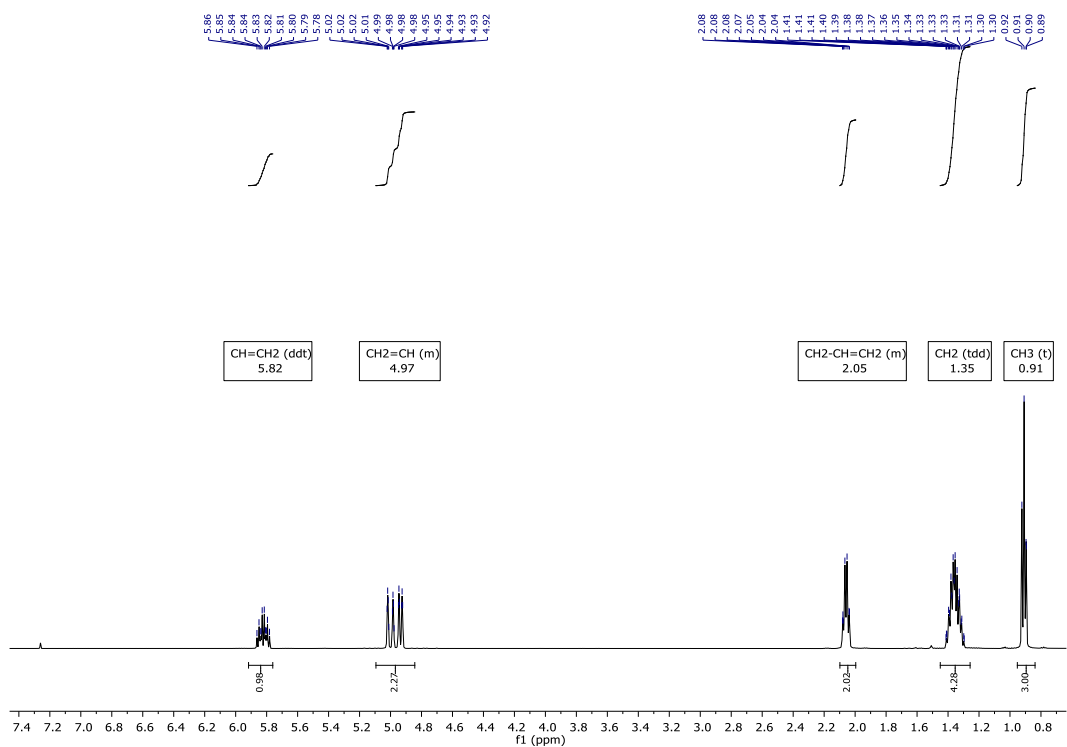


Figure 2: $^1\text{H-NMR}$ spectrum of 1-hexene in CDCl_3 .

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ (ppm) = 5.84 (ddt, J = 16.9, 10.1, 6.7 Hz, 1H, $\text{CH}=\text{CH}_2$), 5.09 – 4.87 (m, 2H, $\text{CH}=\text{CH}_2$), 2.10 – 2.00 (m, 2H, CH_2), 1.45 – 1.26 (m, 4H, CH_2), 0.91 (t, J = 7.1 Hz, 3H, CH_3).

2-hexene:

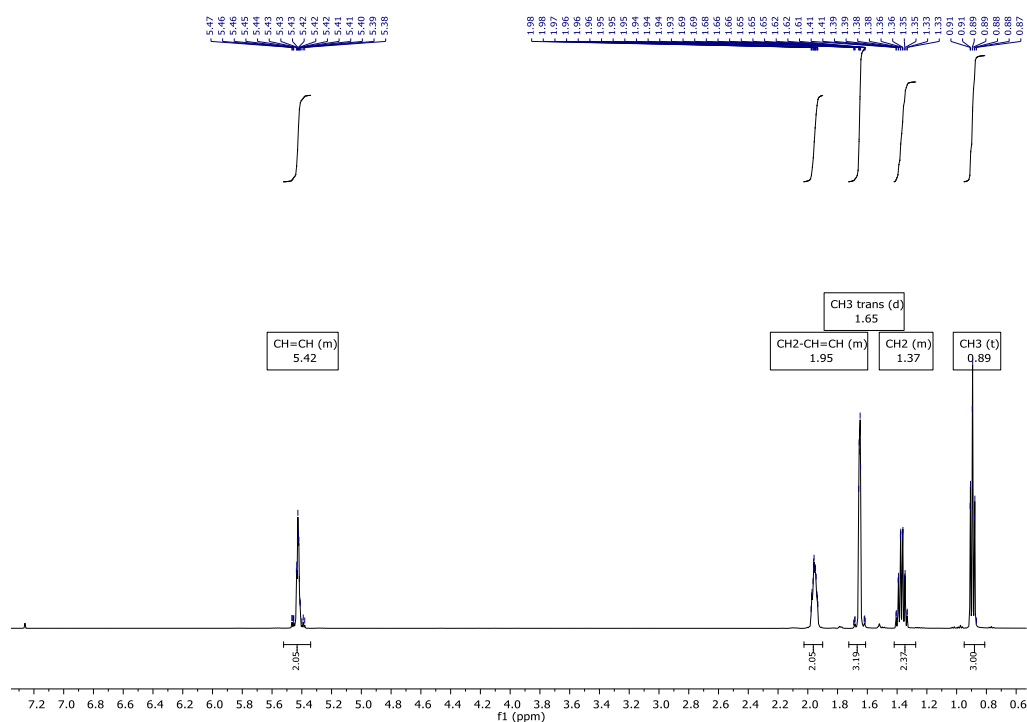


Figure 3: $^1\text{H-NMR}$ spectrum of *trans*-2-hexene in CDCl_3 .

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ (ppm) = 5.52 – 5.34 (m, 2H, $\text{CH}=\text{CH}$), 2.03 – 1.90 (m, 2H, $\text{CH}_2-\text{CH}=\text{CH}$), 1.65 (d, $J = 3.36$ Hz, 3H, $\text{CH}=\text{CH}-\text{CH}_3$), 1.42 – 1.28 (m, 2H, CH_2), 0.89 (t, $J = 7.3, 1.1$ Hz, 3H, CH_3).

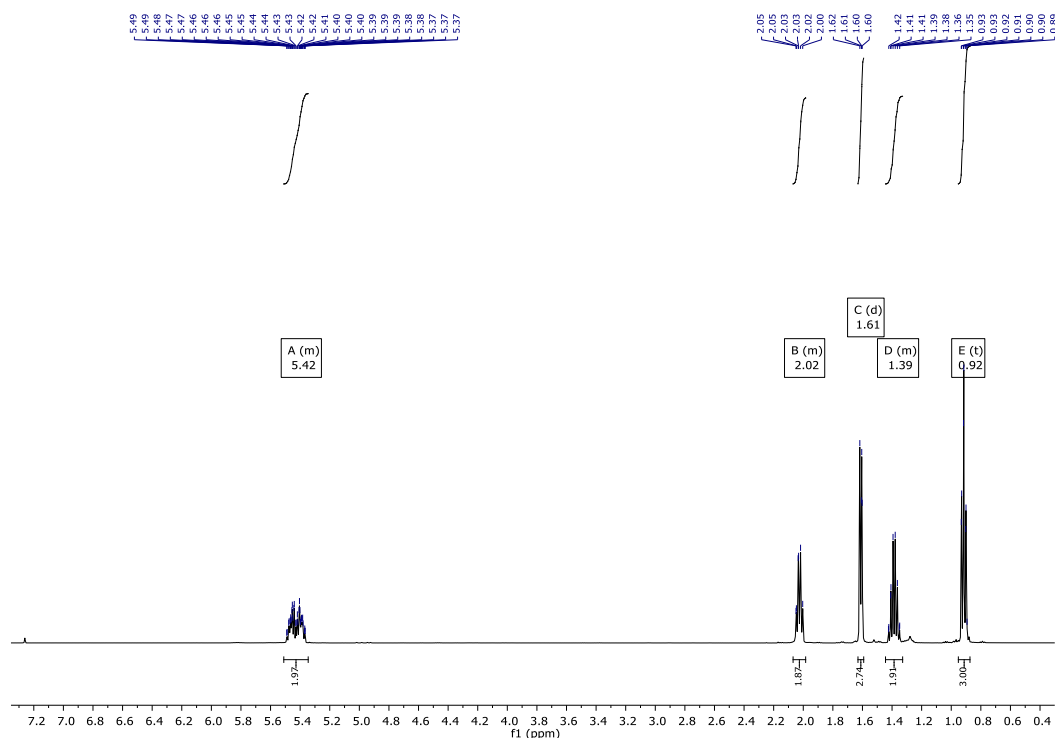


Figure 4: $^1\text{H-NMR}$ spectrum of *cis*-2-hexene.

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ (ppm) = 5.51 – 5.35 (m, 2H, $\text{CH}=\text{CH}$), 2.07 – 1.98 (m, 2H, $\text{CH}_2-\text{CH}=\text{CH}$), 1.61 (d, $J = 6.72$ Hz, 3H, $\text{CH}=\text{CH}-\text{CH}_3$), 1.44 – 1.33 (m, 2H, CH_2), 0.92 (t, $J = 7.4, 3\text{H}$, CH_3).

3-hexene:

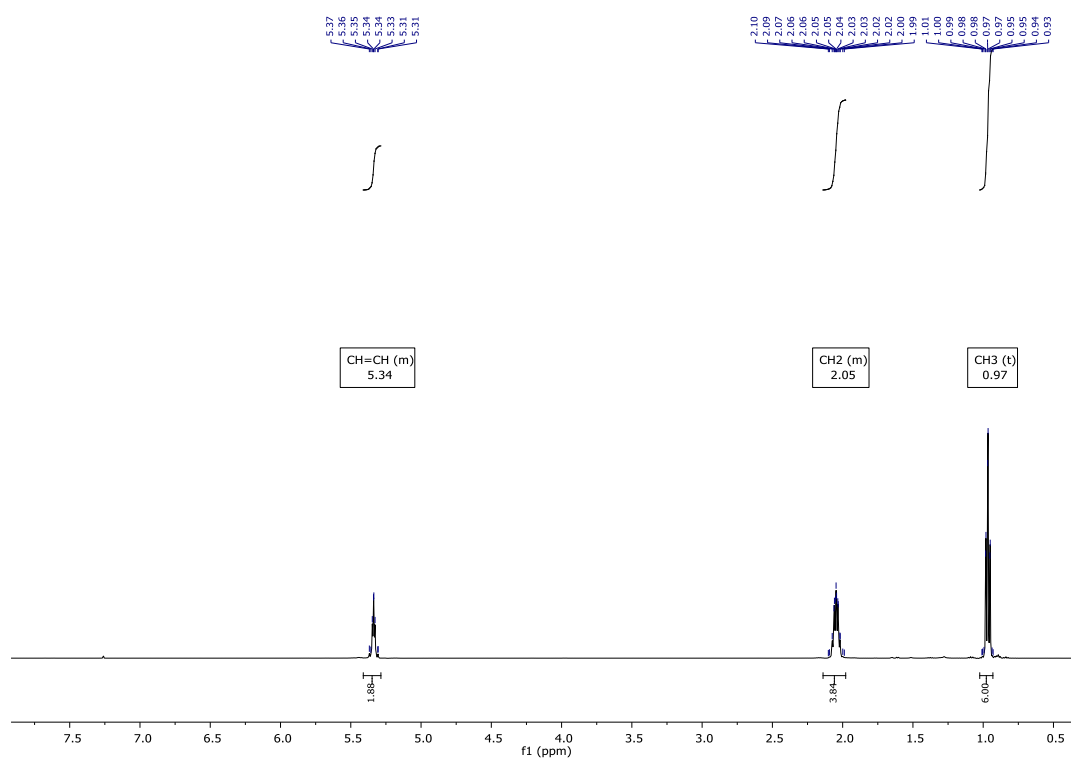


Figure 5: $^1\text{H-NMR}$ spectrum of 3-hexene.

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ (ppm) = 5.41 – 5.29 (m, 2H, $\text{CH}=\text{CH}$), 2.14 – 1.98 (m, 4H, CH_2), 0.97 (t, $J = 7.6$, 6H, CH_3).

di-*n*-hexyl ether:

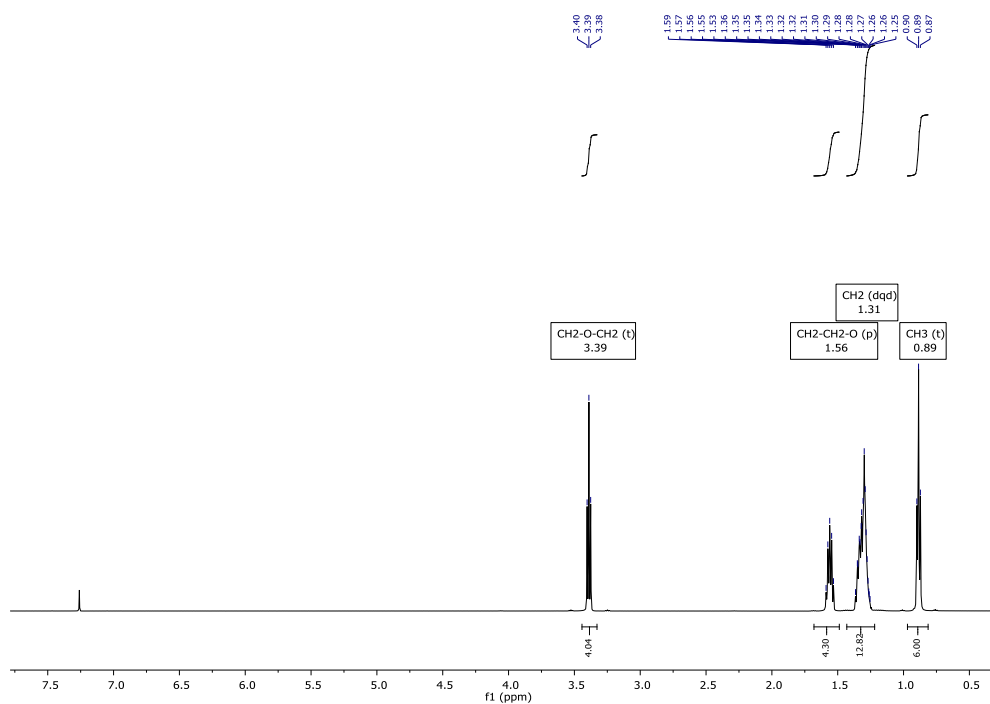


Figure 6: $^1\text{H-NMR}$ spectrum di-*n*-hexyl ether.

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ (ppm) = 3.39 (t, $J = 6.7$ Hz, 4H, $\text{CH}_2\text{-O-CH}_2$), 1.55 (q, $J = 7.0$ Hz, 4H, $\text{CH}_2\text{-CH}_2\text{-O-CH}_2\text{-CH}_2$), 1.31 (dddd, $J = 15.2, 10.9, 7.1, 2.7$ Hz, 12H, CH_2), 0.89 (t, $J = 6.7$ Hz, 3H, CH_3).

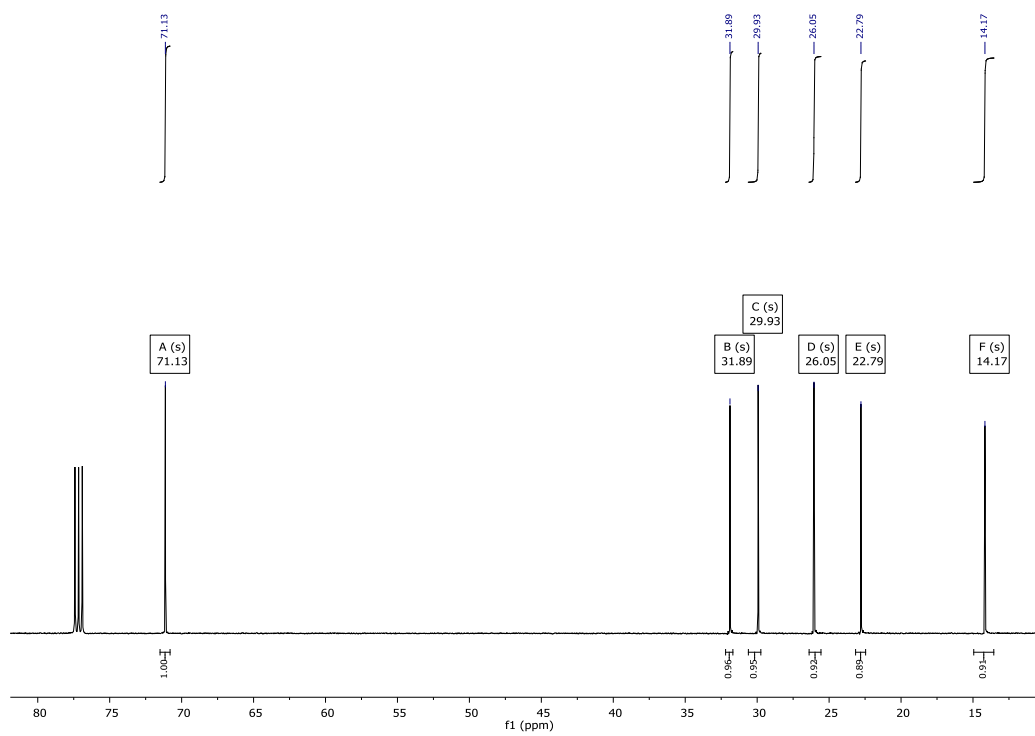
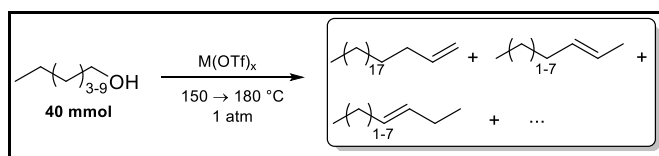


Figure 7: ^{13}C -NMR spectrum of di-*n*-hexyl ether.

^{13}C -NMR (500 MHz, CDCl_3): δ (ppm) = 71.13, 31.89, 29.93, 26.05, 22.79, 14.17.

Dehydration of C₆ – C₁₂ primary alcohols by Cu(OTf)₂ and Hf(OTf)₄



The alcohol (40 mmol) was put together with a catalyst (2 - 10 mol%) in a 25 mL round flask and connected to a micro distillation bridge. It was first heated 1.5 hour at 150 °C then to 180 °C. For alcohols C₈ – C₁₂ the pressure was reduced. After the distillation was finished after 6 h two phases were obtained. Through a separation of the organic phase from the water phase the crude yield was obtained. The crude yield and the hexene purity were then determined through ¹H-NMR spectras.

Table 2: Dehydration of C₆-C₁₂ primary alcohols by Cu(OTf)₂ and Hf(OTf)₄ at 180 °C oil bath temperature..

| alcohol | Cat / mol% | Cat. / g or mL | pressure | Crude yield | Alkene yield |
|-----------------------------|--------------------------------|-------------------|----------------|-------------|--------------|
| 1-hexanol 40 mM 5 mL | 10 mol% | 1.44 g | atmosph. | 81 % | 73 % |
| | Cu(OTf) ₂ | | | 82 % | 75 % |
| | 2 mol% | 0.62 g | | 79 % | 72 % |
| | Hf(OTf) ₄ 2 mol% | 0.52 g | | | |
| 1-heptanol 40 mM 5 mL | 10 mol% | 1.44 g | atmosph. | 76 % | 71 % |
| | Cu(OTf) ₂ | | | 88 % | 84 % |
| | 2 mol% | 0.62 g | | 76 % | 74 % |
| | Hf(OTf) ₄ 2 mol% | 0.52 g | | | |
| 1-octanol 40 mM | 10 mol% | 1.44 g | 550 – 600 mbar | 78 % | 74 % |
| | Cu(OTf) ₂ | | | 73 % | 69 % |
| | 2 mol% | 0.62 g | | 70 % | 62 % |
| | Hf(OTf) ₄ 2 mol% | 0.52 g | | | |
| 1-nonanol 40 mmol | 10 mol% | 1.44 g | 350 – 400 mbar | 65 % | 65 % |
| | Cu(OTf) ₂ | | | 62 % | 61 % |
| | 2 mol% | 0.62 g | | 72 % | 50 % |
| | Hf(OTf) ₄ 2 mol% | 0.52 g | | | |
| 1-decanol 40 mmol | 10 mol% | 1.44 g | 250 -300 mbar | 68 % | 64 % |
| | Cu(OTf) ₂ | | | 70 % | 67 % |
| | 2 mol% | 0.62 g | | 64 % | 52 % |
| | Hf(OTf) ₄ 2 mol% | 0.52 g | | | |
| 1-undecanol 40 mmol | 10 mol% | 1.44 g | 150 – 200 mbar | 55 % | 55 % |
| | Cu(OTf) ₂ | | | 45 % | 45 % |
| | 2 mol% | 0.62 g | | 44 % | 28 % |
| | Hf(OTf) ₄ 2 mol% | 0.52 g | | | |
| 1-dodecanol 40 mmol | 10 mol% | 1.44 g | 100 - 120 mbar | NA | NA |
| | Cu(OTf) ₂ | | | 32 % | 32 % |
| | 2 mol% | 0.62 g | | NA | NA |
| | Hf(OTf) ₄ 2 mol% | 0.52 g | | | |

1-hexene:

¹H-NMR (500 MHz, CDCl₃): δ (ppm) = 5.84 (ddt, J = 16.9, 10.1, 6.7 Hz, 1H, CH=CH₂), 5.09 – 4.87 (m, 2H, CH=CH₂), 2.10 – 2.00 (m, 2H, CH₂), 1.45 – 1.26 (m, 4H, CH₂), 0.91 (t, J = 7.1 Hz, 3H, CH₃).

trans 2-hexene:

¹H-NMR (500 MHz, CDCl₃): δ (ppm) = 5.52 – 5.34 (m, 2H, CH=CH), 2.03 – 1.90 (m, 2H, CH₂-CH=CH), 1.65 (d, J = 3.36 Hz, 3H, CH=CH-CH₃), 1.42 – 1.28 (m, 2H, CH₂), 0.89 (t, J = 7.3, 1.1 Hz, 3H, CH₃).

cis 2-hexene:

¹H-NMR (500 MHz, CDCl₃): δ (ppm) = 5.51 – 5.35 (m, 2H, CH=CH), 2.07 – 1.98 (m, 2H, CH₂-CH=CH), 1.61 (d, J = 6.72 Hz, 3H, CH=CH-CH₃), 1.44 – 1.33 (m, 2H, CH₂), 0.92 (t, J = 7.4, 3H, CH₃).

3-hexene:

¹H-NMR (500 MHz, CDCl₃): δ (ppm) = 5.41 – 5.29 (m, 2H, CH=CH), 2.14 – 1.98 (m, 4H, CH₂), 0.97 (t, J = 7.6, 6H, CH₃).

1-heptene:

¹H-NMR (500 MHz, CDCl₃): δ (ppm) = 5.82 (ddt, J = 17.0, 10.3, 6.7 Hz, 1H, CH=CH₂), 5.04 – 4.88 (m, 2H, CH=CH₂), 2.09 – 2.00 (m, 2H, CH₂-CH=CH₂), 1.59 – 1.48 (m, 6H, CH₂), 0.91 (t, J = 7.24 Hz, 3H, CH₃).

trans 2-heptene:

¹H-NMR (500 MHz, CDCl₃): δ (ppm) = 5.51 – 5.34 (m, 2H, CH=CH), 1.99 – 1.92 (m, 2H, CH₂-CH=CH), 1.64 (d, J = 4.0 Hz, 3H, CH=CH-CH₃), 1.34 – 1.25 (m, 4H, CH₂), 0.89 (t, J = 7.3, 1.1 Hz, 3H, CH₃).

cis 2-heptene:

¹H-NMR (500 MHz, CDCl₃): δ (ppm) = 5.51 – 5.34 (m, 2H, CH=CH), 2.09 – 2.00 (m, 2H, CH-CH=CH), 1.60 (d, J = 6.2 Hz, 3H, CH=CH-CH₃), 1.43 – 1.34 (m, 4H, CH₂), 0.96 (t, J = 7.64 Hz, 3H, CH₃).

3-heptene:

¹H-NMR (500 MHz, CDCl₃): δ (ppm) = 5.41 – 5.29 (m, 2H, CH=CH), 2.14 – 1.98 (m, 4H, CH₂), 1.34 – 1.25 (m, 2H, CH₂), 0.96 (t, J = 7.37 Hz, 3H, CH₃), 0.90 (t, J = 7.6 Hz, 3H, CH₃).

1-octene:

¹H-NMR (500 MHz, CDCl₃): δ (ppm) = 5.82 (ddt, J = 16.9, 10.1, 6.6 Hz, 1H, CH=CH₂), 4.96 (dd, J = 32.4, 13.6 Hz, 2H, CH=CH₂), 2.04 (q, J = 7.1 Hz, 2H, CH₂), 1.38 (dq, J = 14.6, 7.3, 6.6 Hz, 2H, CH₂), 1.33 – 1.23 (m, 6H, CH₂), 0.89 (t, J = 6.6 Hz, 3H, CH₃).

trans 2-octene:

¹H-NMR (500 MHz, CDCl₃): δ (ppm) = 5.42 (td, J = 6.6, 5.8, 3.7 Hz, 2H, CH=CH), 2.01 – 1.88 (m, 2H, CH₂), 1.64 (d, J = 4.1 Hz, 3H, CH₃), 1.40 – 1.15 (m, 6H, CH₂), 0.88 (t, J = 6.9 Hz, 3H, CH₃).

cis 2-octene:

¹H-NMR (500 MHz, CDCl₃): δ (ppm) = 5.42 (td, J = 6.6, 5.8, 3.7 Hz, 2H, CH=CH), 2.08 – 1.99 (m, 2H, CH₂), 1.60 (d, J = 6.1 Hz, 3H, CH₃), 1.40 – 1.15 (m, 6H, CH₂), 0.97 (t, J = 7.4 Hz, 3H, CH₃).

3-octene:

¹H-NMR (500 MHz, CDCl₃): δ (ppm) = 5.53 – 5.34 (m, 2H, CH=CH), 1.99 (dq, J = 12.0, 6.9 Hz, 4H, CH₂), 1.42 – 1.27 (m, 4H, CH₂), 0.96 (t, J = 7.4 Hz, 3H, CH₃), 0.89 (d, J = 7.0 Hz, 3H, CH₃).

4-octene:

¹H-NMR (500 MHz, CDCl₃): δ (ppm) = 5.36 (m, 2H, CH=CH), 2.07 – 1.92 (m, 4H, CH₂), 1.44 – 1.23 (m, 4H, CH₂), 0.88 (t, J = 7.5 Hz, 6H, CH₃).

1-nonene:

¹H-NMR (500 MHz, CDCl₃): δ (ppm) = 5.81 (ddt, J = 17.1, 10.1, 6.7 Hz, 1H, CH=CH₂), 5.04 – 4.89 (m, 2H, CH=CH₂), 2.07 – 2.00 (m, 2H, CH₂), 1.39 – 1.32 (m, 2H, CH₂), 1.33 – 1.23 (m, 8H, CH₂), 0.89 (t, J = 6.6 Hz, 3H, CH₃).

trans 2-nonene:

¹H-NMR (500 MHz, CDCl₃): δ (ppm) = 5.39 (ddt, J = 17.6, 15.4, 5.9 Hz, 2H, CH=CH), 2.00 – 1.92 (m, 2H, CH₂), 1.64 (d, J = 4.2 Hz, 3H, CH₃), 1.33 – 1.23 (m, 8H, CH₂), 0.88 (t, J = 7.3 Hz, 3H, CH₃).

cis 2-nonene:

¹H-NMR (500 MHz, CDCl₃): δ (ppm) = 5.39 (ddt, J = 17.6, 15.4, 5.9 Hz, 2H, CH=CH), 2.07 – 2.0 (m, 2H, CH₂), 1.60 (d, J = 6.1 Hz, 3H, CH₃), 1.39 – 1.32 (m, 8H, CH₂), 0.96 (t, J = 7.2 Hz, 3H, CH₃).

1-decene:

¹H-NMR (500 MHz, CDCl₃): δ (ppm) = 5.91 – 5.75 (m, 1H, CH=CH₂), 4.96 (dd, J = 32.5, 13.6 Hz, 2H, CH=CH₂), 2.08 – 2.00 (m, 2H, CH₂), 1.38 – 1.21 (m, 12H, CH₂), 0.88 (t, J = 6.6 Hz, 3H, CH₃).

trans 2-decene:

¹H-NMR (500 MHz, CDCl₃): δ (ppm) = 5.48 – 5.33 (m, 2H, CH=CH), 2.00 – 1.93 (m, 2H, CH₂), 1.64 (d, J = 4.3 Hz, 3H, CH₃), 1.39 – 1.20 (m, 10H, CH₂), 0.88 (t, J = 7.2 Hz, 3H, CH₃).

cis 2-decene:

¹H-NMR (500 MHz, CDCl₃): δ (ppm) = 5.48 – 5.33 (m, 2H, CH=CH), 2.05 – 2.00 (m, 2H, CH₂), 1.60 (d, J = 6.4 Hz, 3H, CH₃), 1.39 – 1.20 (m, 10H, CH₂), 0.96 (t, J = 7.6 Hz, 3H, CH₃).

1-undecene:

¹H-NMR (500 MHz, CDCl₃): δ (ppm) = 5.87 – 5.77 (m, 1H, CH=CH₂), 4.96 (dd, J = 29.0, 17.3 Hz, 2H, CH=CH₂), 2.08 – 2.00 (m, 2H, CH₂), 1.40 – 1.29 (m, 14H, CH₂), 0.88 (t, J = 6.8 Hz, 3H, CH₃).

trans 2-undecene:

¹H-NMR (500 MHz, CDCl₃): δ (ppm) = 5.49 – 5.29 (m, 2H, CH=CH), 2.00 – 1.92 (m, 2H, CH₂), 1.64 (d, J = 4.2 Hz, 3H, CH₃), 1.40 – 1.29 (m, 12H, CH₂), 0.89 (d, J = 7.1 Hz, 3H, CH₃).

cis 2-undecene:

¹H-NMR (500 MHz, CDCl₃): δ (ppm) = 5.49 – 5.29 (m, 2H, CH=CH), 2.08 – 2.00 (m, 2H, CH₂), 1.60 (d, J = 6.1 Hz, 3H, CH₃), 1.40 – 1.29 (m, 12H, CH₂), 0.96 (t, J = 7.1 Hz, 3H, CH₃).

1-dodecene:

¹H-NMR (500 MHz, CDCl₃): δ (ppm) 5.88 – 5.77 (m, 1H, CH=CH₂), 4.96 (dd, *J* = 32.3, 13.4 Hz, 2H, CH=CH₂), 2.06 – 2.01 (m, 2H, CH₂), 1.40 – 1.31 (m, 16H, CH₂), 0.88 (t, *J* = 7.0 Hz, 3H, CH₃).

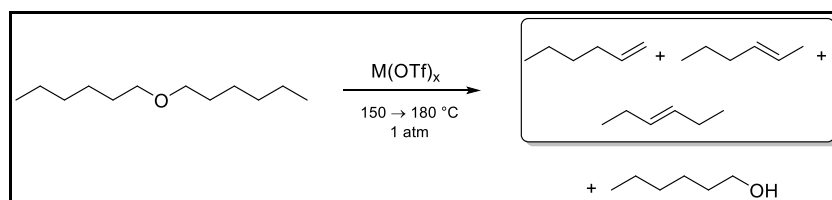
trans 2-dodecene:

¹H-NMR (500 MHz, CDCl₃): δ (ppm) = 5.48 – 5.29 (m, 2H, CH=CH), 1.99 – 1.92 (m, 2H, CH₂), 1.64 (d, *J* = 4.2 Hz, 3H, CH₃), 1.31 – 1.21 (m, 14H, CH₂), 0.88 (t, *J* = 7.0 Hz, 3H, CH₃).

cis 2-dodecene:

¹H-NMR (500 MHz, CDCl₃): δ (ppm) = 5.48 – 5.29 (m, 2H, CH=CH), 2.06 – 2.01 (m, 2H, CH₂), 1.60 (d, *J* = 6.1 Hz, 3H, CH₃), 1.40 – 1.31 (m, 14H, CH₂), 0.96 (t, *J* = 7.4 Hz, 3H, CH₃).

Dehydration of di-*n*-hexyl ether:



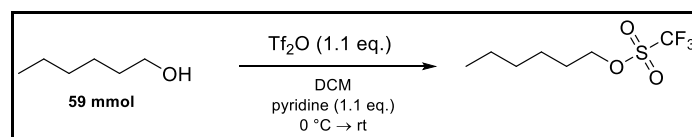
The ether (22 mmol) was put together with a catalyst (4 - 20 mol%) in a 25 mL round flask and connected to a micro distillation bridge. It was first heated 1.5 hour at 150 °C then to 180 °C. After the distillation was finished after 6 h two phases were obtained. Through a separation of the organic phase from the water phase the crude yield was obtained. The crude yield and the hexene purity were then determined through ¹H-NMR spectras.

Table 3: Dehydration of C₆-C₁₂ primary alcohols by Cu(OTf)₂ and Hf(OTf)₄ at 180 °C oil bath temperature.

| entry | catalyst | catalyst loading / mol% | catalyst loading/ g | substrate | substrate loading / mmol | substrate loading / mL | alkene yield / % |
|-------|----------|-------------------------|---------------------|---------------------------|--------------------------|------------------------|------------------|
| 1 | | 10 | 1.44 g | 1-hexanol | 40 | 5 mL | 73 |
| 2 | Cu(II) | 20 | 1.44 g | di- <i>n</i> -hexyl ether | 22 | 5 mL | 68 |
| 3 | | 20 | 1.44 g | di- <i>n</i> -hexyl ether | 22 | 5 mL | 71 ^a |
| 4 | | 2 | 0.62 g | 1-hexanol | 40 | 5 mL | 75 |
| 5 | Hf(IV) | 4 | 0.62 g | di- <i>n</i> -hexyl ether | 22 | 5 mL | 66 |
| 6 | | 4 | 0.62 g | di- <i>n</i> -hexyl ether | 22 | 5 mL | 67 ^a |

^a 0.5 eq. of water was used to enhance the reaction.

Synthesis of 1-hexyl triflate:



1-hexyl triflate was synthesized accordingly to literature.² 160 mL of dry dichloromethane and triflic anhydride (11 mL, 66 mmol, 1.1 eq.) were presented in a 500 mL round flask. Afterwards 1-hexanol (7.5 mL, 59 mmol, 1 eq.) and dry pyridine (5.4 mL, 66 mmol, 1.1 eq.) in 80 mL dichloromethane were dripped to the reaction mixture under constant stirring and ice bath cooling for 1 h. Afterwards, the reaction mixture was stirred at rt for 3 h. The reaction was quenched by the adding of 120 mL dH_2O . The organic phase was separated from the aqueous phase. Then the organic phase was washed with 120 mL water. The aqueous phase was extracted with 120 mL dichloromethane. The united organic phases were dried by Na_2SO_4 , and the solvent removed under reduced pressure. 1-hexyl triflate was obtained as a viscous dark coloured oil with a yield of 88 %.

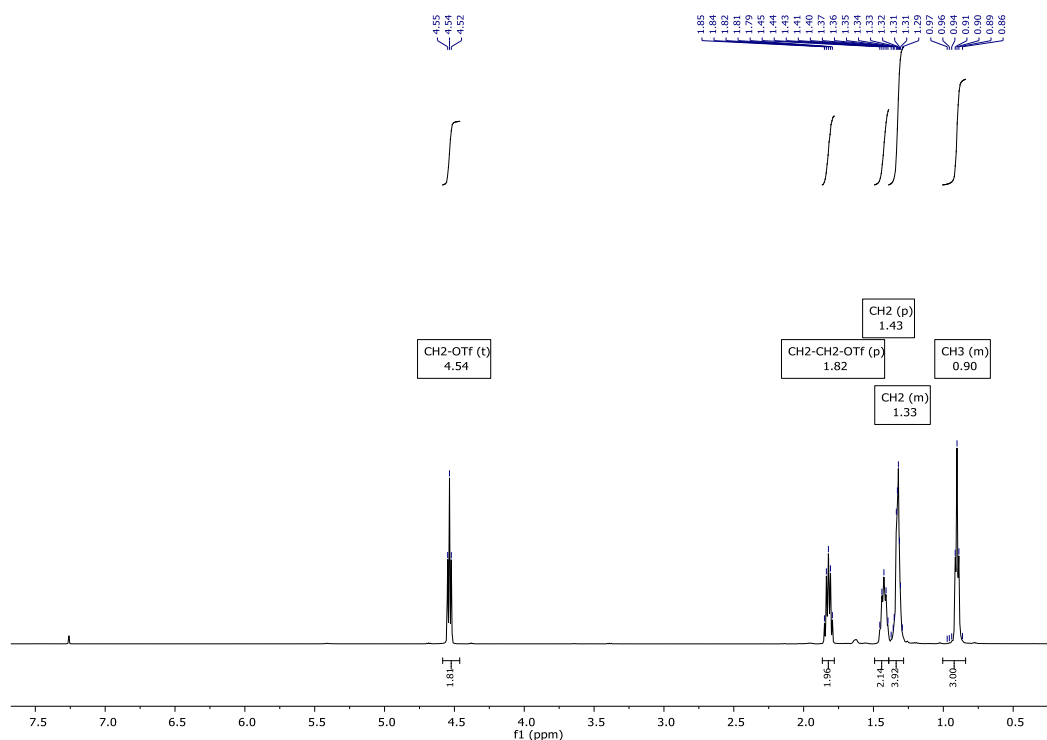


Figure 8: $^1\text{H-NMR}$ spectrum of 1-hexyl triflate in CDCl_3 .

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ (ppm) = 4.54 (t, $J = 6.6$ Hz, 2H), 1.82 (p, $J = 6.8$ Hz, 2H), 1.43 (p, $J = 7.1$ Hz, 2H), 1.39 – 1.28 (m, 4H), 1.00 – 0.84 (m, 3H).

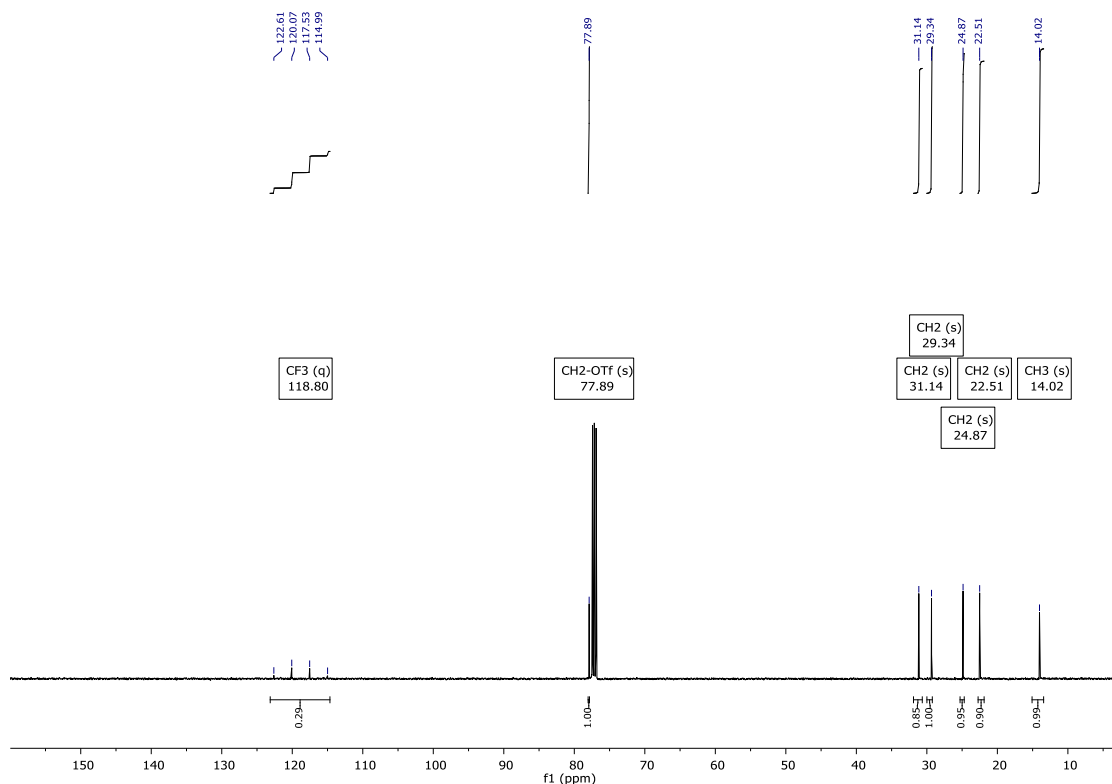


Figure 9: ^{13}C -NMR spectrum of 1-hexyl triflate.

^{13}C -NMR (500 MHz, CDCl_3): δ (ppm) = 118.80, 77.89, 31.14, 29.34, 24.87, 22.51, 14.02.

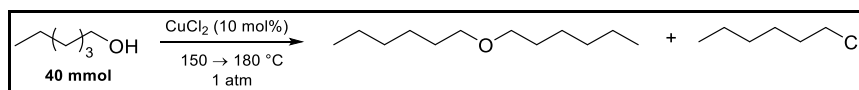
Reactions with 1-hexyl triflate

To investigate 1-hexyl triflate as a possible intermediate candidate in the dehydration of 1-hexanol by metal triflates different approaches were taken. In almost all approaches 1-hexyl triflate (40 mmol) was presented in a 25 mL round flask and connected to a distillation bridge. In the next step either additives or no additives (method a) were added. For method b) and c) either 10 mol% $\text{Cu}(\text{OTf})_2$ or 1 eq. 1-hexanol were added, respectively. Just in case of method d) an excess of EtOH under reflux was used. For method a) – c) only decomposition products were obtained. Only for method d) the ether was formed. In neither cases a modest amount of alkene was formed.

Table 4: Elimination of 1-hexyl triflate to the ether and corresponding alkenes by: a) just heating hexyltriflate under distillation, b) adding Cu(OTf)₂ under distillation, c) adding triflic acid under distillation, d) using same amount of 1-hexanol (1) under distillation and e) using an excess of ethanol under reflux.

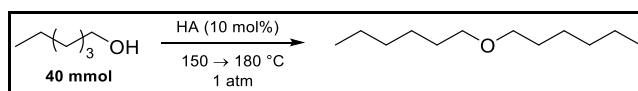
| Approach | Method | Additive | Oil bath temperature | Conversion to ether or alkenes | Main product |
|----------|-----------------------------|---------------------------------|----------------------|----------------------------------|------------------------|
| a) | just heating up | - | 110 °C | no | decomposition products |
| b) | adding Cu(OTf) ₂ | 10 mol% Cu(OTf) ₂ | 110 °C | no | decomposition products |
| c) | adding 1-hexanol | 1 eq. 1-hexanol | 110 – 180 °C | small amount of hexene (<<< 1 %) | decomposition products |
| d) | Excess EtOH under reflux | 10 mL EtOH | Reflux | quant. ether formation | ethylhexylether |

Dehydration of 1-hexanol by CuCl₂



1-hexanol (40 mmol, 5 mL) was presented with CuCl₂ (10 mol%, 4 mmol, 0.54 g) in a 25 mL round flask and connected to a micro distillation bridge. It was first heated for 1.5 hours at 150 °C then to 180 °C for additional 4.5 h. After the reaction was terminated both, the crude mixture and the distillation flask were investigated by ¹H-NMR. As products only hexyl chloride with a yield of 4 % and di-*n*-hexyl ether with a yield of 19 % were found whereby only in the distillation flask hexyl chloride was determined.

Dehydration of 1-hexanol by Brønsted acids



1-hexanol (40 mmol) was presented together with a Brønsted acid (10 mol%) in a 25 mL round flask and connected to a micro distillation bridge. It was first heated 1.5 hour at 150 °C then to 180 °C. After 22 h the reaction was terminated. The crude mixture was measured by $^1\text{H-NMR}$. When the ether was formed, the crude mixture was filtered using a celite column and then purified using a silica column and cyclohexene as an eluent. After evaporation of the solvent the yield and purity were determined.

Table 5: Dehydration of 1-hexanol using Brønsted acids.

| entry | Brønsted acid | catalyst loading / mol% | pKa | substrate loading / mmol | substrate loading / mL | Ether yield / % | alkene yield / % |
|-------|-------------------------|-------------------------|-------|--------------------------|------------------------|-----------------|------------------|
| 1 | acetic acid | 10 | 4.8 | 40 | 5 | not formed | |
| 2 | H_3PO_4 | 10 | 2.1 | 40 | 5 | not formed | |
| 3 | trifluoroacetic acid | 10 | 0.23 | 40 | 5 | not formed | |
| 4 | tosylic acid | 10 | - 2.8 | 40 | 5 | 96 | not formed |
| 5 | H_2SO_4 | 10 | - 3 | 40 | 5 | 86 | not formed |

OC1_AllahverdiyevAd_1222_AA4Air2123_saeule_3.1.fid

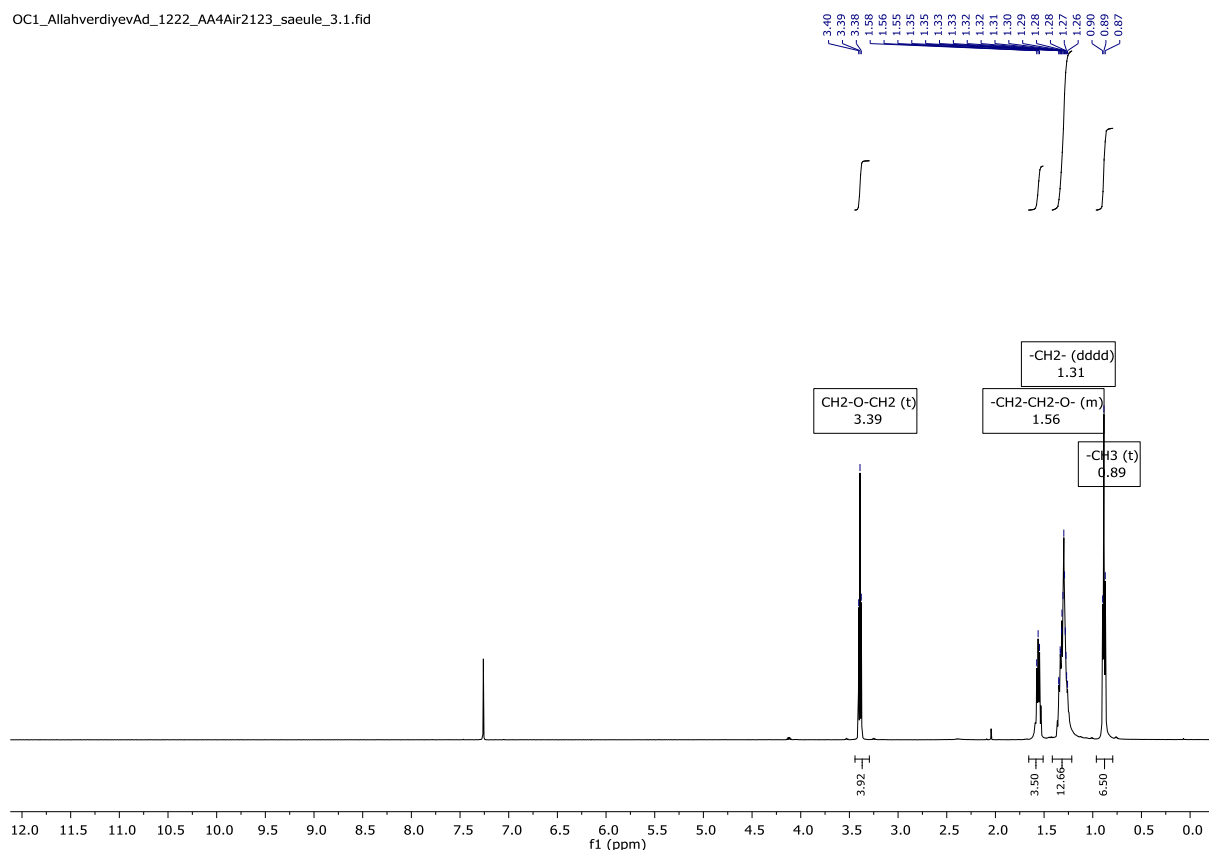
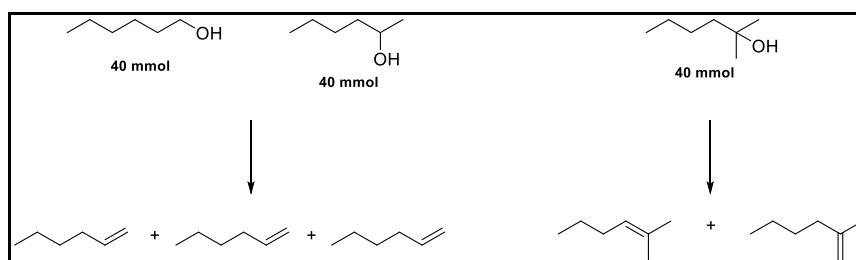


Figure 10: $^1\text{H-NMR}$ spectrum of di-*n*-hexyl ether in CDCl_3 . After synthesis by H_2SO_4 and column chromatography.

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ (ppm) = 3.39 (t, J = 6.7 Hz, 4H, $-\text{CH}_2\text{-O-CH}_2-$), 1.66 – 1.51 (m, 4H, $-\text{CH}_2\text{-CH}_2\text{-O-}$), 1.31 (dddd, J = 19.2, 15.6, 7.7, 3.3 Hz, 12H, $-\text{CH}_2-$), 0.89 (t, J = 6.8 Hz, 6H, $-\text{CH}_3$).

Dehydration of primary, secondary and tertiary alcohols



The alcohol (40 mmol) was presented together with a LEWIS acid (10 mol%) in a 25 mL round flask and connected to a micro distillation bridge. In case of the primary alcohol it was first heated 1.5 hour at 150 °C then to 180 °C. In case of the secondary and tertiary alcohol the temperature was increased to 110 °C or 150 °C and held, respectively. After the reaction finished the organic phase was separated from the water phase and then was measured by $^1\text{H-NMR}$. When the ether was formed, the crude mixture was filtered using a celite column and then purified using a silica column and cyclohexene as an eluent. After evaporation of the solvent the yield and purity were determined.

In case of the tertiary alcohol 83 % of SAYTZEFF and 17 % of HOFMANN product was obtained.

Table 6: Dehydration of primary, secondary and tertiary alcohols by $\text{Hf}(\text{OTf})_4$ (2 mol%) and $\text{Cu}(\text{OTf})_2$ (10 mol%).

| Substrate | $T_{\text{oil}} / ^\circ\text{C}$ | t / h | alkene yield / % | |
|-----------|-----------------------------------|-------|------------------|--------|
| | | | Hf(IV) | Cu(II) |
| | 180 | 6 | 75 | 75 |
| | 150 | 3 | 89 | 92 |
| | 110 | 0.5 | 86 | 83 |

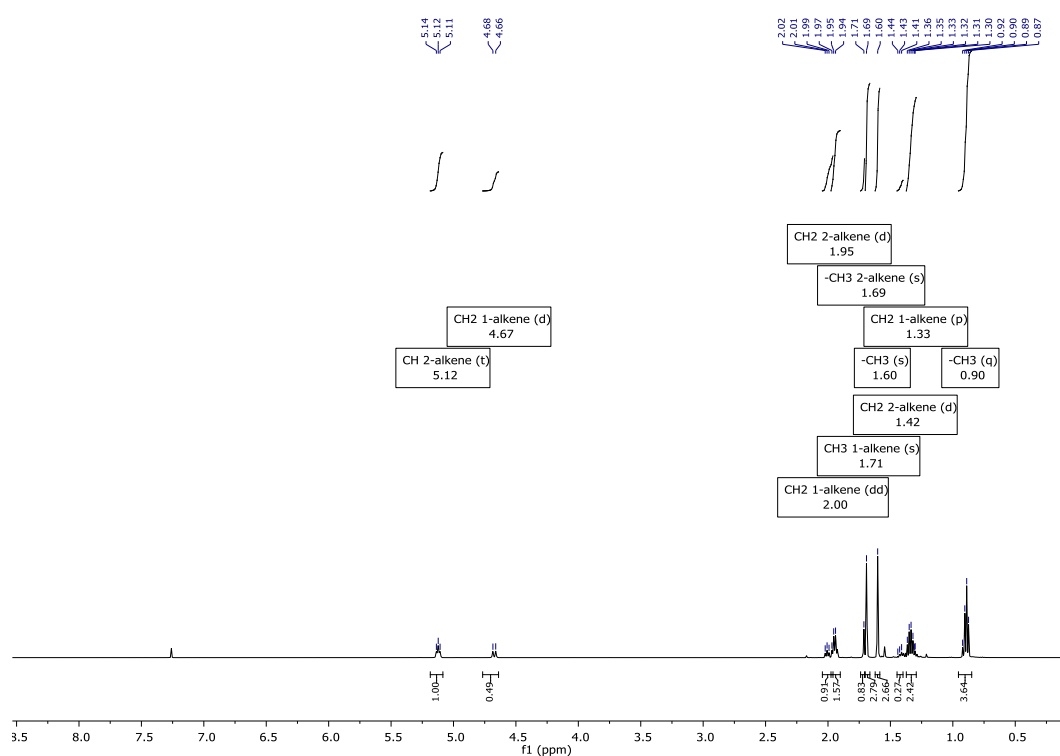


Figure 11: $^1\text{H-NMR}$ spectrum of 2-methyl-1-hexene and 2-methyl-2-hexene in CDCl_3 after the dehydration of 2-methyl-2-hexanol by $\text{Hf}(\text{OTf})_4$.

2-Methyl-1-hexene:

¹H NMR (500 MHz, Chloroform-*d*): δ 5.12 (t, *J* = 7.4 Hz, 1H, -CH-), 1.95 (d, *J* = 7.4 Hz, 2H, -CH₂-CH), 1.69 (s, 3H, -CH₃), 1.60 (s, 3H, -CH₃), 1.33 (p, *J* = 8.7, 8.1 Hz, 2H, CH₂-CH₃), 0.90 (q, *J* = 8.1, 7.4 Hz, 3H, -CH₃).

2-Methyl-2-hexene:

¹H NMR (500 MHz, Chloroform-*d*): δ 4.67 (d, *J* = 11.2 Hz, 2H, -CH₂=CH₂), 2.00 (dd, *J* = 17.4, 9.6 Hz, 2H, -CH₂=CH₂), 1.71 (s, 3H, -CH₃), 1.42 (d, *J* = 7.8 Hz, 4H, -CH₂-), 0.90 (q, *J* = 8.1, 7.4 Hz, 3H).

Calculation of Sustainability Metrics

The sustainability metrics were calculated using the following equations.

$$E - factor = \frac{mass_{waste}}{mass_{product}} \cdot 100\% \quad (1)$$

$$PMI = \frac{mass_{total}}{mass_{product}} \cdot 100\% \quad (2)$$

with $mass_{waste}$, $mass_{product}$ and m_{total} describing the mass of the waste and product as well as the total mass.

DFT calculations

All quantum chemical calculations were generated by using the ORCA software package.³ Geometries were calculated at the PBE0 D3BJ def2-TZVP def2/J level of theory in the gas phase. Frequency calculations at the same level were performed for the validation of each structure as a minimum or a transition state, followed by single-point calculations. IRC (internal reaction coordinate) calculations starting from the transition structures were performed for the verification of the reactants and products.

DFT-optimized Cartesian coordinates

Optimized Cartesian coordinates for H₂SO₄

| | | | |
|---|-------------------|------------------|-------------------|
| S | -3.92760606960994 | 1.88363292403929 | -1.73201235476062 |
| O | -3.04314009856564 | 0.57425430563789 | -1.77012980594888 |
| H | -2.60930627774506 | 0.51373414748952 | -2.63241376472721 |
| O | -5.26869988234357 | 1.40165723744979 | -2.41527491440351 |
| H | -5.82081084230621 | 0.96859780156339 | -1.74977614244221 |
| O | -3.36846840674382 | 2.83633742706563 | -2.61807222089260 |
| O | -4.18158842268575 | 2.13265615675449 | -0.36146079682497 |

Optimized Cartesian coordinates for Cu(OTf)₂

| | | | |
|----|-------------------|-------------------|-------------------|
| Cu | 0.54185608847571 | -0.16202371587961 | -0.28681962315360 |
| O | -0.91539737566553 | -1.47241086312175 | -0.11154702194940 |

| | | | |
|---|-------------------|-------------------|-------------------|
| S | -1.96930257997765 | -0.39913664949371 | 0.02730819241750 |
| O | -1.13386862992832 | 0.85430782426702 | -0.08838162430720 |
| C | -2.93913529091359 | -0.46903358010437 | -1.54058143872514 |
| F | -3.52154443741183 | -1.64845938973932 | -1.62559337464278 |
| F | -3.85302444906561 | 0.48019457657160 | -1.51760212989176 |
| O | -2.91117753965366 | -0.50205149027699 | 1.09754324619755 |
| F | -2.13908200366375 | -0.29193479771645 | -2.57791054503641 |
| O | 2.00746781859251 | 1.14489914679268 | -0.42351685872608 |
| S | 3.06114251124113 | 0.06816352353609 | -0.53609365263727 |
| O | 2.21574633605793 | -1.18225081418076 | -0.46772513757918 |
| C | 3.96621172051097 | 0.11197070892689 | 1.07175153550946 |
| F | 4.87339241749019 | -0.84373089448828 | 1.07882612874393 |
| F | 4.55415923350927 | 1.28442218849986 | 1.19794955887652 |
| O | 4.04337523705663 | 0.17730303941390 | -1.56888192585072 |
| F | 3.11704094334558 | -0.07070881300678 | 2.06866467075458 |

Optimized Cartesian coordinates for ethanol

| | | | |
|---|-------------------|------------------|-------------------|
| C | -4.88823923825288 | 2.94365253873076 | 0.05370132003692 |
| C | -6.19447527334319 | 2.18057723925784 | 0.06541514628726 |
| O | -7.25229664460519 | 3.10779627896298 | 0.10605144687630 |
| H | -6.21189166892559 | 1.50686157615996 | 0.93357277247334 |
| H | -6.24792406107720 | 1.54234073316632 | -0.82780425546743 |
| H | -8.08215385427094 | 2.62748112351342 | 0.11282727625201 |
| H | -4.82555750306358 | 3.59910228389906 | -0.81489650666602 |
| H | -4.04600309393240 | 2.25301160498478 | 0.01622490261991 |
| H | -4.78320866252903 | 3.55605662132487 | 0.94916789758771 |

Optimized Cartesian coordinates for transition state A with sulfuric acid

| | | | |
|---|-------------------|-------------------|------------------|
| O | -0.36981905093363 | -1.51828546486117 | 3.06062821541132 |
| O | -0.02119151293001 | 0.62306365355366 | 1.88670373996050 |

| | | | |
|---|-------------------|-------------------|-------------------|
| S | -0.36492319344768 | -0.78051405040654 | 1.84470935339019 |
| O | 0.37331170183615 | -1.48503203088390 | 0.75756070867267 |
| O | -1.88448112379739 | -0.73432903512051 | 1.29884402507866 |
| H | -1.58418082294277 | 0.82774577064880 | -0.53806037441383 |
| H | -2.29656902097974 | -1.58663603499656 | 1.48778029485108 |
| H | 0.77655462774738 | -0.75264532556612 | -0.25266238690289 |
| C | 0.72250177704746 | 0.98109616199945 | -1.63438258404682 |
| H | 0.04082647525671 | 1.03832592820203 | -2.47309990130263 |
| H | 1.12791319829973 | 1.93211015432071 | -1.31501030968038 |
| O | -0.87802101094577 | 1.48112698609490 | -0.45908230787201 |
| C | 1.34719750193075 | -0.21183856920366 | -1.29252113188977 |
| H | 2.33613866316559 | -0.11805733870814 | -0.84879203773666 |
| H | -0.54667928836060 | 1.34167327115719 | 0.46633549024495 |
| H | 1.22142107905378 | -1.03780407623014 | -1.98895079376437 |

Optimized Cartesian coordinates for transition state B with cooper triflate

| | | | |
|----|-------------------|-------------------|-------------------|
| Cu | 0.69051836027654 | -1.05792347934222 | 1.18047098700458 |
| O | -0.62561553712979 | -1.72879387364338 | 0.10142816065268 |
| S | -1.98589200533865 | -1.12545010957695 | 0.44884291452919 |
| O | -1.74081706454342 | 0.07528282023021 | 1.24653047938227 |
| C | -2.56650247561732 | -0.52708613911913 | -1.22083926401248 |
| F | -2.83443840608580 | -1.56817149961865 | -1.97066412932081 |
| F | -3.64763961025369 | 0.19118073619200 | -1.01879812730216 |
| O | -2.90721953808685 | -2.08067132214251 | 0.95359999569265 |
| F | -1.61887679528799 | 0.20456748406857 | -1.76135357829594 |
| O | 2.08659784296513 | -0.20407419722674 | 2.11360114432766 |
| S | 2.61889238171466 | 0.48046676029772 | 0.87380703844999 |
| O | 1.56854093925184 | 0.02851098757211 | -0.10438260005036 |
| C | 4.16467654316486 | -0.46199859917653 | 0.44124480264565 |
| F | 4.64189244974211 | 0.01949237947700 | -0.67730475456034 |
| F | 5.01510344237065 | -0.30685598331763 | 1.42595341017686 |

| | | | |
|---|-------------------|-------------------|------------------|
| O | 2.91529422767729 | 1.85263975098527 | 0.95758622346001 |
| F | 3.84728790646833 | -1.73539542191021 | 0.30152128192800 |
| O | 0.06542027690706 | -1.94734360365308 | 2.59068258390491 |
| C | -1.47504549621538 | -1.14991695759482 | 4.32430668328156 |
| C | -2.36238237342547 | -0.15822495851484 | 3.94787777508578 |
| H | -3.40895831531902 | -0.43314491380378 | 3.83046254955925 |
| H | -2.15122269560450 | 0.86153470032385 | 4.26174393138979 |
| H | -1.99380484364093 | -0.15821707948458 | 2.80507623663447 |
| H | -1.75250298586247 | -2.19753157464625 | 4.26949838639935 |
| H | -0.48786500608038 | -0.92543990917854 | 4.71202109289947 |
| H | -0.31103122204666 | -2.78011599719601 | 2.26962677613614 |

Literature

- 1 a) I. Hachiya, M. Moriwaki and S. Kobayashi, *Tetrahedron Letters*, 1995, **36**, 409–412; b) J. Keskiväli, A. Parviainen, K. Lagerblom and T. Repo, *RSC Adv.*, 2018, **8**, 15111–15118;
- 2 T. Hartman, J. Šturala and R. Cibulka, *Adv. Synth. Catal.*, 2015, **357**, 3573–3586.
- 3 Calculations were carried out using the ORCA 5.3.0 software; F. Neese, The ORCA program system, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2012, **2**, 73-78.