Electronic Supplementary Material

Energy-Saving Dehydration of Alcohols Through Modified Spanish Attapulgites as Catalysts for a Sustainable Synthesis of Industrially Relevant Alkene Chemicals

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General conditions

Chemicals were commercially bought and used without any further purification. Reactions were performed under atmospheric pressure and air. Reactions were generally carried out under neat conditions and reactive distillation to shift the equilibrium towards the product site.

Dehydration of 1-hexanol by non-activated and activated Red Attapulgite

1-hexanol (5 mL, 40 mmol) was presented in a 25 mL flask which was connected to a micro-distillation bridge. 40 wt% of the catalyst was used. To avoid premature distillation of the substrate due to the low boiling point (157 °C), the reaction was first heated for 1.5 h to an oil bath temperature of 150 °C, then to 180 °C to enable ether formation and mixing of the catalyst. This resulted in a slightly increased boiling point. Alkene formation was observable by distillation. After a total reaction time of 6 h, the organic phase of the distillation flask was separated from the aqueous phase. The alkene yield was determined by ^{1}H-NMR and weighting of the distillation flask.

Table S1. Dehydration of 1-hexanol (40 mmol) by heterogenous catalysts

entry	catalyst	pKa	loading		alkene yield
			/ mol%	/ wt%	/ %
1	Red Attapulgite, non-activated	NA[a]	NA	40	0
2	Red Attapulgite, acid-pretreated	NA	NA	40	46

[a]not available

Dehydration of secondary alcohols exemplified for 2-hexanol

2-hexanol (40 mmol) was presented in a 25 mL flask which was connected to a micro-distillation bridge. 40 wt% of the catalyst was added. The reaction was heated to 150 °C for 3 h. Alkene formation was observable by distillation. After the end of the reaction, the organic phase of the distillation flask was separated from the aqueous phase. The alkene yield was calculated by ^{1}H-NMR and weighting of the sample.

For the reusability studies, the catalyst and substrate (40 mmol) were first heated at 150 °C for 3 h. Fresh substrate (40 mmol) was then added to initiate the next cycle, and this procedure was repeated four times, resulting in a total of five consecutive reaction cycles. The reaction temperature and duration were kept constants for all cycles.

Table S2. Dehydration of 2-hexanol (40 mmol) using attapulgites.

entry	catalyst	cycle	loading / wt%	alkene yield / %
1	Red Attapulgite, unactivated	1	40	0
2	Red Attapulgite, pretreated	1	40	84
3	Red Attapulgite, pretreated	2	40	86
4	Red Attapulgite, pretreated	3	40	82
5	Red Attapulgite, pretreated	4	40	88
6	Red Attapulgite, pretreated	5	40	86

Dehydration of tertiary alcohols exemplified for 2-methyl-2-hexanol

2-methyl-2-hexanol (40 mmol) was presented in a 25 mL flask which was connected to a micro-distillation bridge. 40 wt% of the catalyst was added. The reaction was heated to 150 °C for 3 h. Alkene formation was observable by distillation. After the end of the reaction, the organic phase of the distillation flask was separated from the aqueous phase. The alkene yield was calculated by ^{1}H-NMR and weighting of the sample.

For the reusability studies, the catalyst and substrate (40 mmol) were first heated at 110 °C for 3 h. Fresh substrate (40 mmol) was then added to initiate the next cycle, and this procedure was repeated four times, resulting in a total of five consecutive reaction cycles. The reaction temperature and duration were kept constants for all cycles.

Table S3. Dehydration of 2-methyl-2-hexanol (40 mmol) using attapulgites.

entry	catalyst	cycle	loading / wt%	alkene yield / %
1	Red Attapulgite, non-activated	1	40	0
2	Red Attapulgite, acid-pretreated	1	40	90
3	Red Attapulgite, acid-pretreated	2	40	95
4	Red Attapulgite, acid-pretreated	3	40	90
5	Red Attapulgite, acid-pretreated	4	40	99
6	Red Attapulgite, acid-pretreated	5	40	91

^{1}H-NMR Data

1-hexene:

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 5.84 (ddt, J = 16.9, 10.1, 6.7 Hz, 1H, C*H*=CH_2), 5.09 – 4.87 (m, 2H, CH=C*H*$_2$), 2.10 – 2.00 (m, 2H, C*H*$_2$), 1.45 – 1.26 (m, 4H, C*H*$_2$), 0.91 (t, J = 7.1 Hz, 3H, C*H*$_3$).

trans 2-hexene:

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

cis 2-hexene:

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

3-hexene:

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 5.41 – 5.29 (m, 2H, C*H*=C*H*), 2.14 – 1.98 (m, 4H, C*H*$_2$), 0.97 (t, *J* = 7.6, 6H, C*H*$_3$).

di-*n*-hexyl ether:

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 3.39 (t, *J* = 6.7 Hz, 4H, C*H*$_2$-O-C*H*$_2$), 1.55 (q, *J* = 7.0 Hz, 4H, C*H*$_2$-CH_2-O-CH_2-C*H*$_2$), 1.31 (dddd, *J* = 15.2, 10.9, 7.1, 2.7 Hz, 12H, C*H*$_2$), 0.89 (t, *J* = 6.7 Hz, 3H, C*H*$_3$).

2-Methyl-1-hexene:

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 4.68, 4.66 (2 br s, 2H, -CH_2-C(CH_3)=C*H*$_2$), 2.00 (t, J = 9.6 Hz, 2H, -C*H*$_2$-C=CH_2), 1.71 (s, 3H, -CH_2-C(C*H*$_3$)=CH_2), 1.46 – 1.37 (m, 4H, -C*H*$_2$-), 0.90 (t, J = 8.1, 7.4 Hz, 3H, -CH_2-C*H*$_3$)

2-Methyl-2-hexene:

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 5.12 (t, J = 7.4 Hz, 1H, -C*H*-), 1.95 (dt, J = 7.4, 14.3 Hz, 2H, -C*H*$_2$-CH), 1.69 (s, 3H, -C*H*$_3$), 1.60 (s, 3H, -C*H*$_3$), 1.37 – 1.28 (m, 2H, -C*H*$_2$-CH_3), 0.90 (t, J = 7.4 Hz, 3H, -C*H*$_3$).

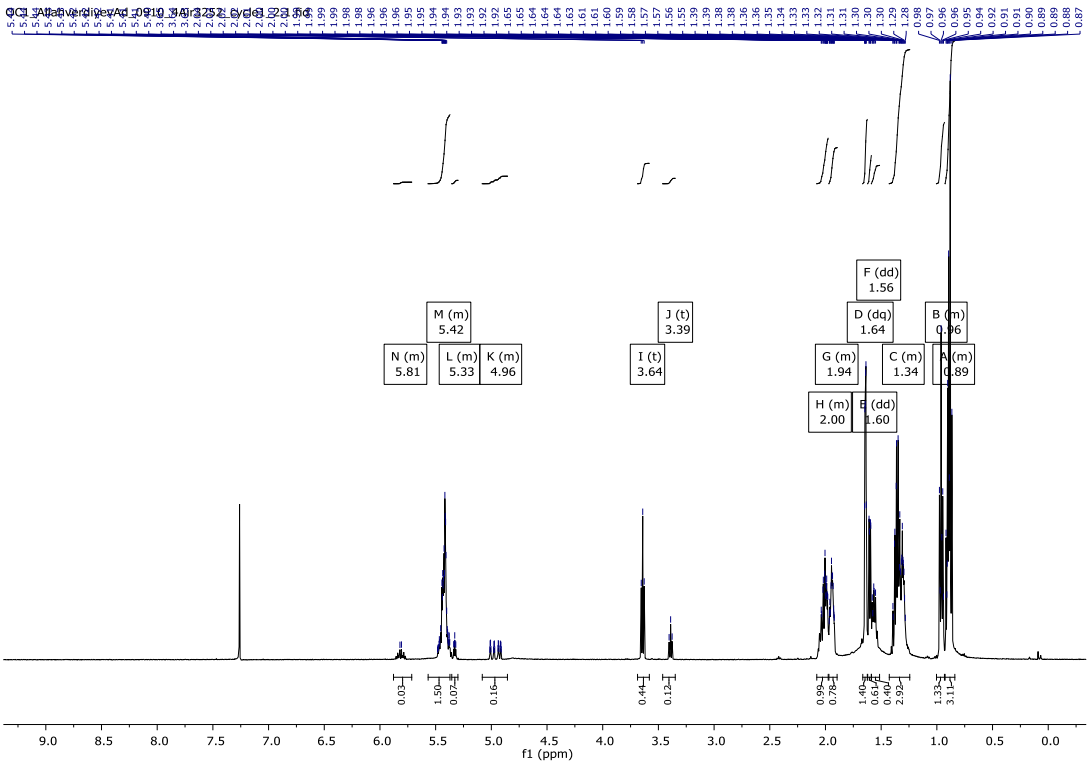


Figure S1. ^{1}H-NMR spectrum of the dehydration of 1-hexanol by acid-pretreated Red Attapulgite in $CDCl_3$.

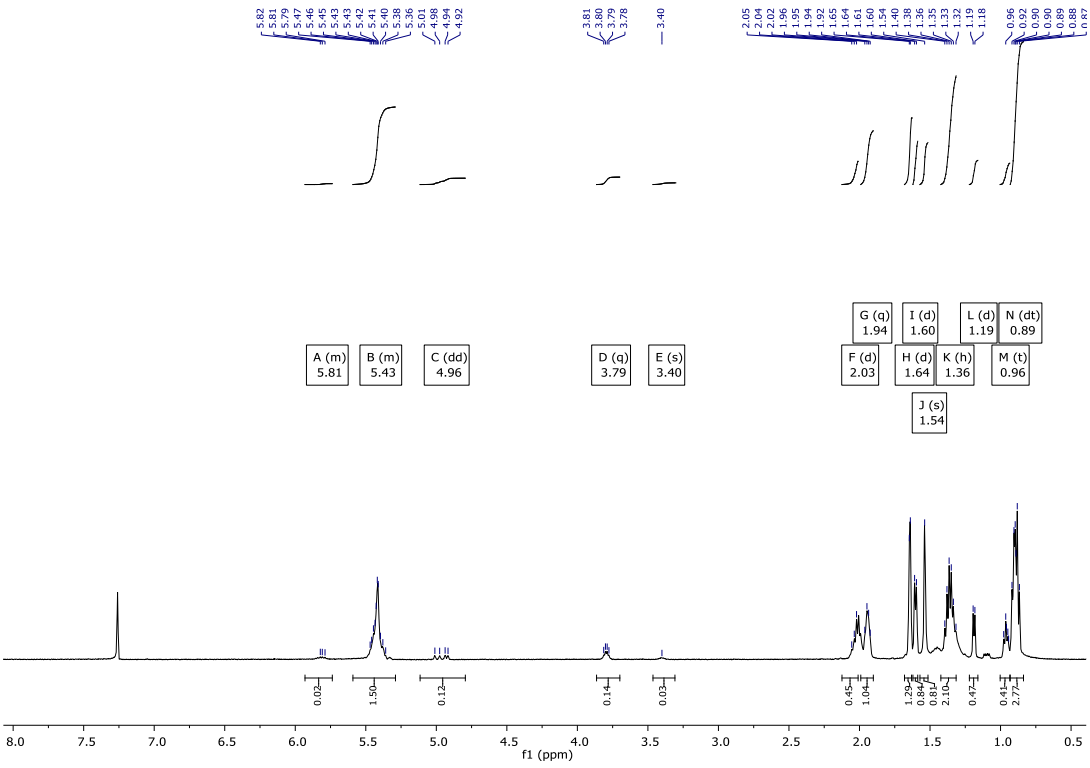


Figure S2. ^{1}H-NMR spectrum of the dehydration of 2-hexanol by acid-pretreated Red Attapulgite in $CDCl_3$.

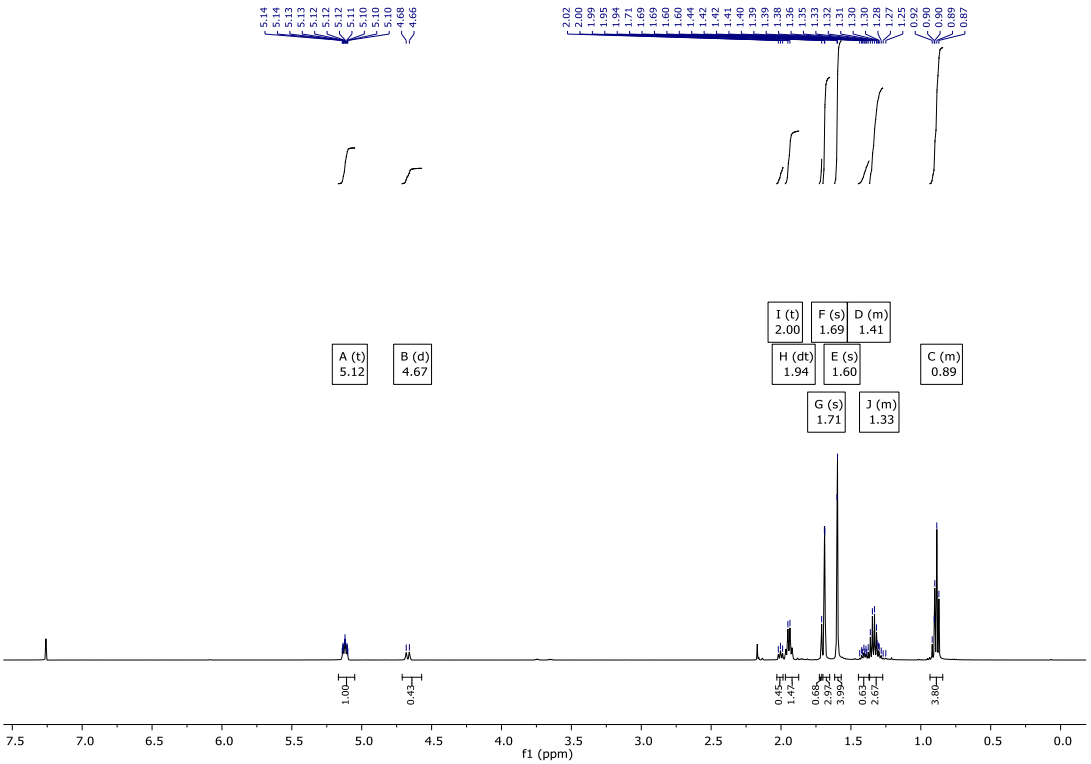


Figure S3. ^{1}H-NMR spectrum of the dehydration of 2-methyl-2-hexanol (40 mmol) by acid-pretreated Red-Attapulgite in $CDCl_3$.

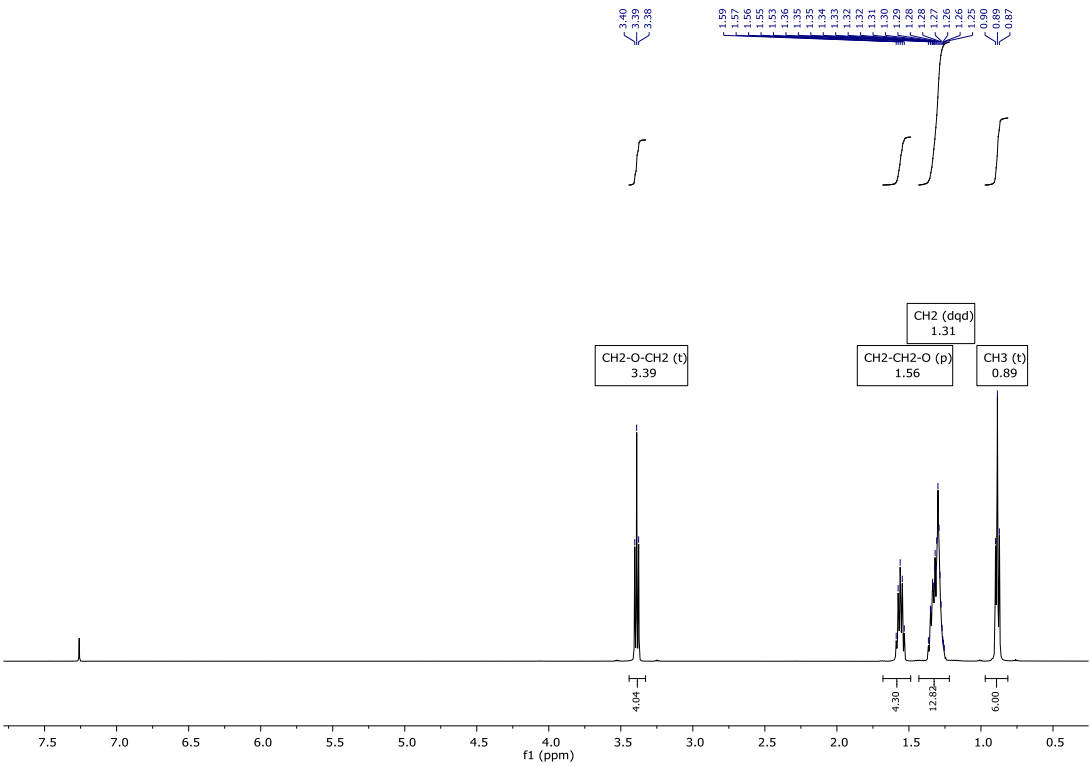


Figure S4. ^{1}H-NMR spectrum di-*n*-hexyl ether in $CDCl_3$.

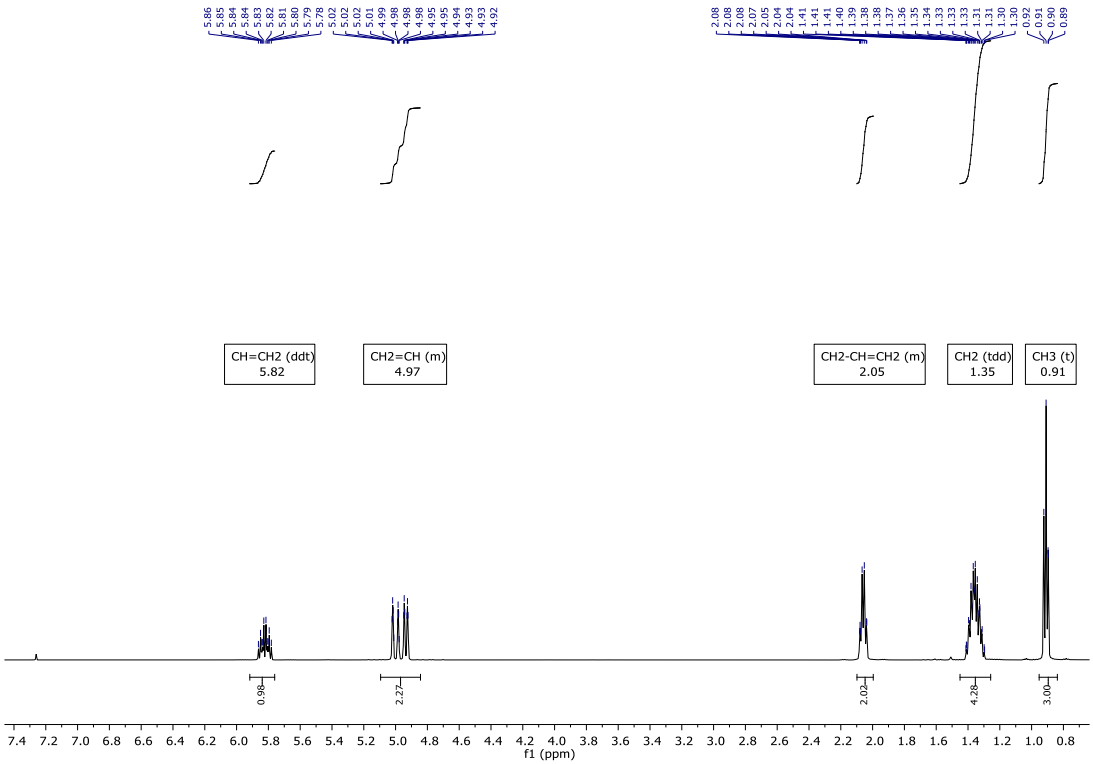


Figure S5. ^{1}H-NMR spectrum of 1-hexene in $CDCl_3$.

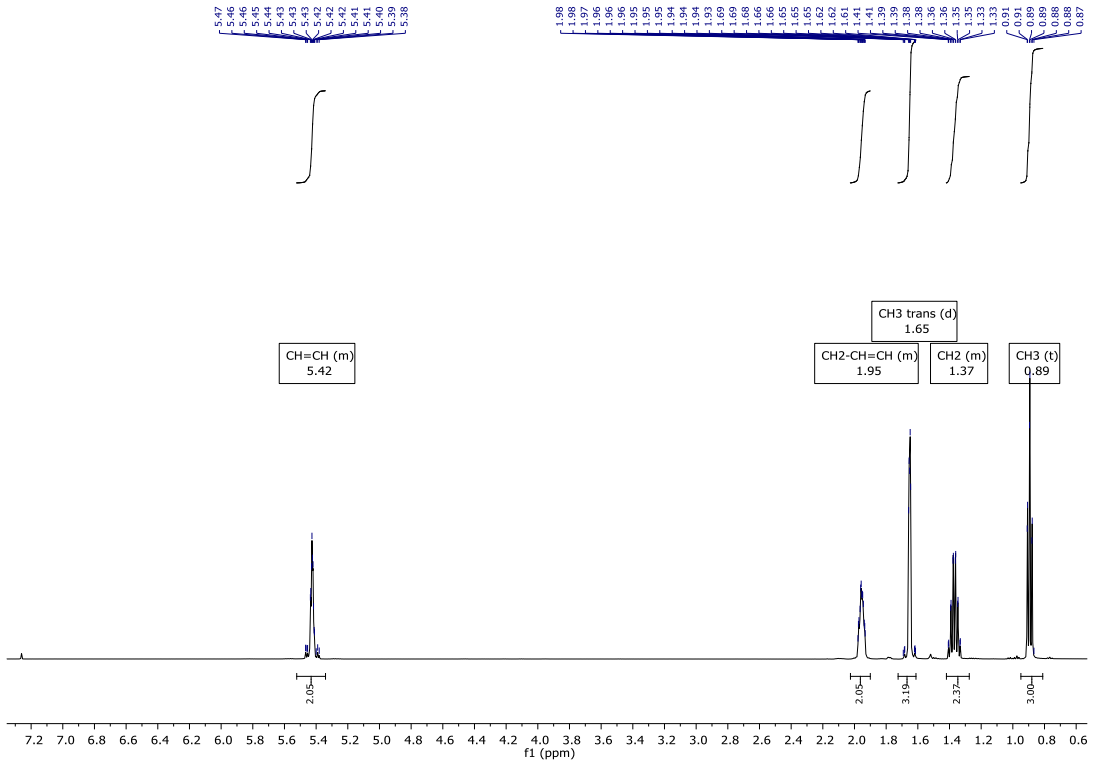


Figure S6. ^{1}H-NMR spectrum of *trans* 2-hexene in $CDCl_3$.

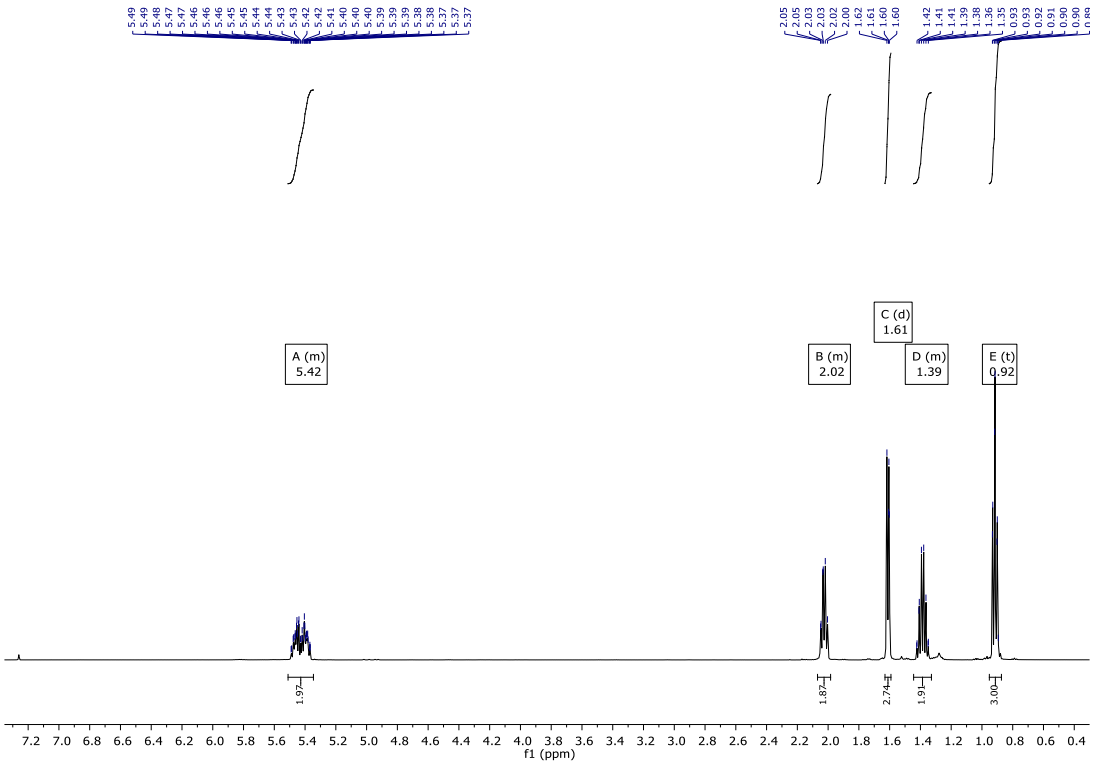


Figure S7. ^{1}H-NMR spectrum of *cis* 2-hexene in $CDCl_3$.

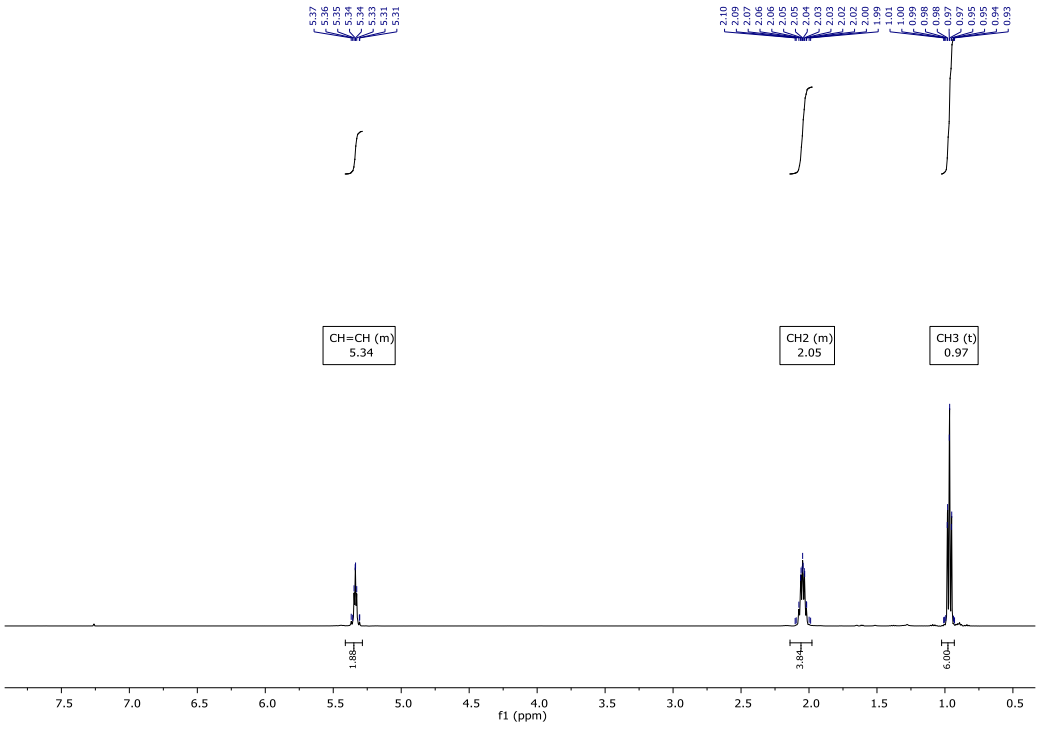


Figure S8. ^{1}H-NMR spectrum of 3-hexene in $CDCl_3$.