



*Citation for published version:*

Coxon, AGN & Kohn, RD 2016, 'Efficient 1-hexene trimerization with triazacyclohexane chromium catalysts and detailed product analysis by  $^{13}\text{C}$  NMR', *ACS Catalysis*, vol. 6, no. 5, pp. 3008-3016.  
<https://doi.org/10.1021/acscatal.6b00542>

*DOI:*

[10.1021/acscatal.6b00542](https://doi.org/10.1021/acscatal.6b00542)

*Publication date:*

2016

*Document Version*

Peer reviewed version

[Link to publication](#)

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## Supporting Information

### Efficient 1-Hexene Trimerization with Triazacyclohexane Chromium Catalysts and Detailed Product Analysis by $^{13}\text{C}$ NMR

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#### Quantitative analysis of product distribution in 1-octene trimerization

A small Schlenk tube is loaded with 1.0mg of **1b** (0.0011mmol) and 21.0mg of DMAO (320eq Al), dissolved in 1g PhF<sub>2</sub> followed by 768.5 mg of 1-octene (stored over NaK, 6.85mmol, 6100eq, contains 0.6w% or 5mg 2-octene and 2.0w% or 15mg 2-Et-1-hexene) and more PhF<sub>2</sub> to rinse the pipette (total 2.11g PhF<sub>2</sub>). The solution was stirred in the glove box for 4hrs, taken out of the box and all volatiles were pumped off at 50mbar (LN<sub>2</sub> trap): 2.04g containing 0.81w% 1-octene (16.5mg), 0.99w% 2-octenes (20mg) and 0.44w% 2-Et-1-hexene (9mg).

120mg of biphenyl is dissolved in 1.5g pentane and washed into the trimerization residue (817mg) with 5g pentane followed by water and HCl. The pentane phase is separated and the aq phase extracted with further pentane to give 15g solution (GCMS, NMR: ca 49mg PhF<sub>2</sub>, 6mg 1-octene, 806mg trimer) which is then reduced at 120mbar/RT for NMR: 750mg trimer, 7mg 1-octene, 12mg PhF<sub>2</sub>.

#### Synthesis of Terminally Labelled 1- $^{13}\text{C}$ -1-Hexene [17]

1 g (7 mmol) of  $^{13}\text{C}$ -enriched methyl iodide was diluted into 20 ml of toluene. The solution was placed into a salted ice bath and cooled to  $-14^\circ\text{C}$ . 1.90 g (7.2mmol) of triphenylphosphine was then dissolved into the solution. The solution was left stirring for one week at RT and a white precipitate gradually crashed out over this period. The toluene was removed under vacuum at  $10^{-2}$  mbar over the course of two hours to give 2.83 g of  $^{13}\text{C}$ -MePPh<sub>3</sub>I in quantitative yield.

0.1731 g (7.2 mmol) of sodium hydride was added followed by 8.5 g of tetraglyme (dried and vacuum distilled from sodium) as solvent which formed a viscous white suspension. This was stirred for 5 days under argon and gradually became a clear dark yellow solution of the ylide.

0.604 g (7 mmol) of valeraldehyde was added by syringe into the ylide solution under nitrogen followed by 1.5 g of *p*-cymene. The solution was left to stir for 4 hours resulting in a white precipitate of the triphenylphosphine oxide by-product. The volatile constituents were vacuum transferred off the white solid to give a solution of 1-hexene in *p*-cymene. A small quantity of  $^i\text{Bu}_3\text{Al}$  is added to bind any residual tetraglyme, aldehyde or moisture followed by a final vacuum transfer. The concentration (and purity) of the solution was determined by NMR analysis and indicated a yield of 443 mg (74%) over all three steps.

$^1\text{H}$  NMR 400MHz, [*p*-cymene: 6.98 (4H, m), 2.75 (1H, m), 2.19 (3H, s), 1.18 (6H, d)]:  $\delta$  = 5.72 (1H, m,  $J$  = 10.2,  $-\text{CHCH}_2$ ), 4.95 (2H, d of d of d,  $J_{\text{CH}} = 152.2$ ,  $=\text{CH}_2$ ), 1.99 (2H, m,  $J$  = 6.5,  $-\text{CH}_2\text{CHCH}_2$ ), 1.30 (4H, m,  $-\text{CH}_2\text{CH}_2\text{CH}_3$ ), 0.88 (3H, t,  $J$  = 6.8,  $-\text{CH}_3$ ).

$^{13}\text{C}$  NMR 100MHz, [*p*-cymene: 145.1, 135.1, 129.4, 126.6, 34.3, 24.5, 21.2]:  $\delta$  = 138.3 (d,  $-\text{CHCH}_2$ ), 114.6 ( $-\text{CH}_2$ ), 34.1 ( $-\text{CH}_2\text{CHCH}_2$ ), 32.6 ( $-\text{CH}_2\text{CH}_2\text{CH}_3$ ), 22.8 ( $-\text{CH}_2\text{CH}_3$ ), 14.3 ( $-\text{CH}_3$ ).

### Synthesis of 2-<sup>13</sup>C-1-hexene

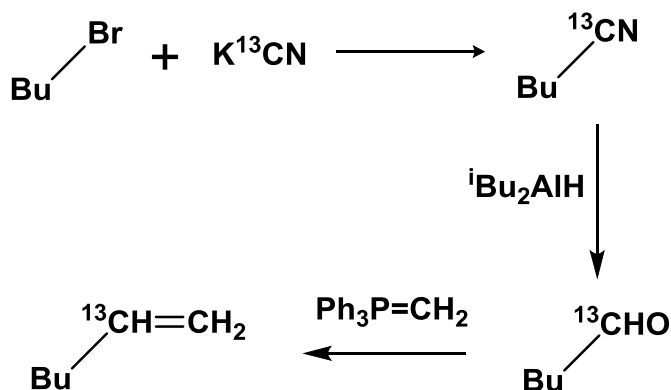


Figure S1. Synthesis of 2-<sup>13</sup>C-1-hexene

K<sup>13</sup>CN (1.01g, 15.3mmol) is combined with Bu<sub>3</sub>N (68mg, 0.37mmol, 0.02eq), 2.0ml 1-bromobutane (d=1.278, 18.7mmol, 1.2eq) and 2.5g water and the mixture is refluxed at 105 °C for 20hrs. The phases are allowed to cool and settle and the organic top phase is collected and combined with DCM extracts of the aqueous phase, washed with water, dried with MgSO<sub>4</sub> and filtered and the solids washed with some heptane. The combined solution is distilled until heptane distils (100 °C). The remaining 3.65g contain about 32w% Bu<sup>13</sup>CN (1.17g, 13.9mmol, 91%) with 0.5g DCM and 0.5g BuBr (3.6mmol) by NMR (neat):

<sup>1</sup>H : 2.20dt (2H, 9.7+7.0Hz), 1.47m (2H), 1.35m (2H), 0.8 (3H)

<sup>13</sup>C: 118.77 (<sup>13</sup>CN), 27.35d (2.7Hz), 21.56d (3.45Hz), 16.27d (55.9Hz), 12.5

The mixture was diluted with more heptane and distilled at 125 °C. A light brown oil separates from the heptane (BuCN not soluble when DCM is gone?).

Check by NMR shows that about 0.8g of Bu<sup>13</sup>CN is in the colourless heptane solution.

The solution is transferred away from the brown oil (5.84g) and checked by NMR again showing 1.01g Bu<sup>13</sup>CN (M=84, 12.0mmol, 79%). A second extraction gave more heptane solution (1.9g containing 92mg clean Bu<sup>13</sup>CN (1.1mmol, total 86% yield).

The combined heptane solutions (13.1mmol) are degassed and cooled to -70 °C and 1M <sup>i</sup>Bu<sub>2</sub>AlH in heptane (12.32g, 16.85ml, d=0.731, 16.85mmol) added drop wise over 30min. The solution is kept stirring below -50 °C for 30min and then slowly to 0 °C over 1hr and placed by an ice bath. After 30min, 25ml of cold 6% HCl is added drop wise over 15min. The aq phase is removed and the organic phase washed with the remaining 50ml 6% HCl, 10ml water, dried over MgSO<sub>4</sub> and rotavapped down. The aqueous phase is extracted with further 10ml heptane, washed with water, dried and combined with the other solution giving a total of 27g solution (3.8w% by NMR, 1.03g, M=86 for Bu<sup>13</sup>CHO, 11.9mmol, 91%).

6.46g (16.0mmol) Ph<sub>3</sub>PMeI and 387mg NaH (16.1mmol) are mixed with 15g tetraglyme and stirred in a glove box for 4d. 845mg are filtered into an NMR tube showing about 13mmol ylid has formed. The rest is filtered (ca 80% of the solution), taken out of box, cooled in an ice bath and the <sup>13</sup>C-valeraldehyde solution in heptane above is added drop wise. Finally the NMR sample of the ylid is combined with the aldehyde solution (still yellow). All volatiles are vacuum transferred into a liquid nitrogen cooled flask followed by partial further transfers. An NMR showed about 230mg hexene (2.7mmol) with some benzene and Et<sub>2</sub>O. An attempt to trimerize this mixture failed (no rx after 6hrs). All volatiles are vacuum transferred off into a small Schlenk tube, transferred onto 400mg <sup>i</sup>Bu<sub>3</sub>Al to bind any Et<sub>2</sub>O or water and transferred back. This solution is checked by NMR and used for trimerization.

### Synthesis of a mixture of A, A', B, and B':

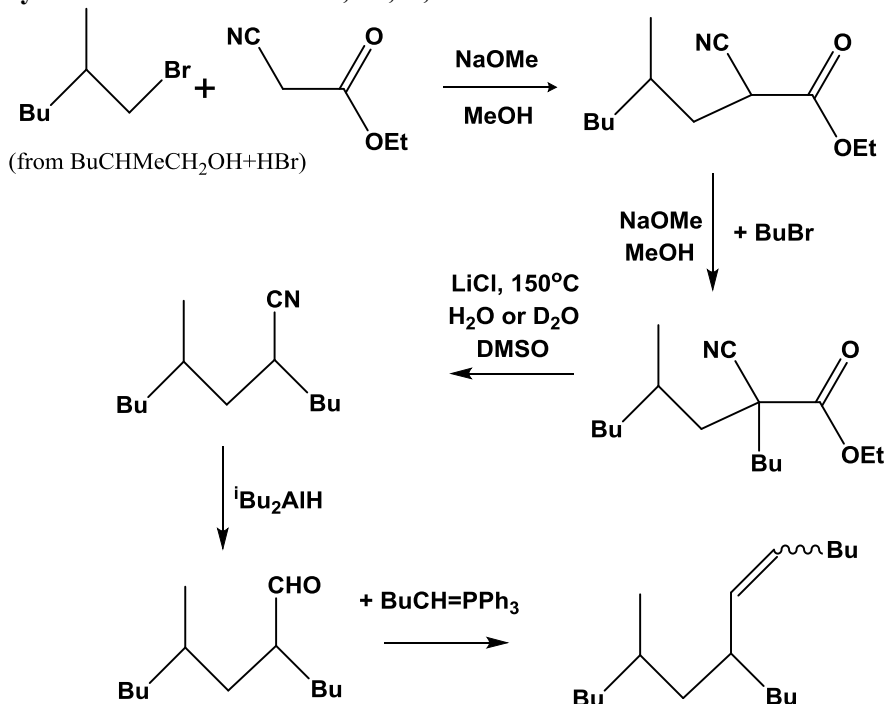


Figure S2. Synthesis of mixture of A, A', B and B'

### Synthesis of 2-methyl-1-hexanol

[according to J.K. Crandall, A.C. Clark, *J. Org. Chem.*, Vol. **37**, 1972]

4.50 g allyl alcohol (77 mmol) is dissolved in 50 mL hexane and cooled in an ice bath. 33 mL 2.5 M n-BuLi in hexane (24.1 g of solution, 34.8 mL, 87 mmol) is added via syringe, followed by 19 mL TMEDA (15.16g) and after stirring for 30 min a further 65 mL of 2.5 M n-BuLi is added. The ice bath was removed after 30 min and stirring continued at RT for 2 hrs. The mixture was cooled in the ice bath again and quenched by the addition of 10 mL water. Stirring the mixture at RT for 30 min resulted in a clear solution over white solids. The solution is decanted into a separation funnel and washed with three portions of dilute HCl. The aqueous phases are decanted and the organic phase is washed with two 30 mL portions of water, dried over MgSO<sub>4</sub> and the solvent is removed under vacuum. The resulting yellow oil is vacuum transferred at 43 mbar at ~300°C to give 6.365g of a colourless liquid (60 mmol, 78%).

<sup>1</sup>H NMR, CDCl<sub>3</sub>: δ = 3.42 + 3.32 (1H each, m, -CH<sub>2</sub>OH), 3.3 (1H, broad s, -OH), 1.54 (1H, octet, J = 5.9, -CHCH<sub>2</sub>OH), 1.35 + 1.03 (1H each, m, -CH<sub>2</sub>Pr), 1.26 (2H, m, CH<sub>2</sub>Et), 1.26 (2H, m, -CH<sub>2</sub>Me), 0.86 (3H, m, -CH<sub>2</sub>CH<sub>3</sub>), 0.85 (3H, d, -CHCH<sub>3</sub>).

<sup>13</sup>C NMR, CDCl<sub>3</sub>: δ = 67.95 (t, J = 140.0, -CH<sub>2</sub>OH), 35.59 (d, J = 123.7, -CHCH<sub>2</sub>OH), 32.79 (t, J = 123.7, -CH<sub>2</sub>Pr), 29.11 (t, J = 125.2, -CH<sub>2</sub>Et), 22.87 (3-Bu, t, J = 125.4, -CH<sub>2</sub>Me), 16.46 (q"sext", 124.9 / 4.3, -CHCH<sub>3</sub>), 13.92 (q, J = 124.3, -CH<sub>2</sub>CH<sub>3</sub>).

### Synthesis of 2-methyl-1-bromohexane

[according to *Patent: US5476649 A1, 1995*]

6.3 g of 2-methyl-1-hexanol (54.8 mmol) are dissolved in 8.0 mL 48% HBr and 2.0 mL conc. H<sub>2</sub>SO<sub>4</sub> and heated for 2 days at 105°C. The mixture went dark brown. After cool water (30 mL)

was added, the mixture was extracted with three 30 mL portions of pentane which were then dried over MgSO<sub>4</sub>. The solvent was removed in vacuo and the oil transferred at 1mbar and ~300°C to give 7.669 g (86w% with rest remaining alcohol, 37 mmol, 67% yield) of a colourless liquid.

NMR in CDCl<sub>3</sub>:

<sup>1</sup>H (7.27): 3.398dd (1H, 4.92+9.77Hz), 3.326dd (1H, 6.26+9.77Hz), 1.787ddtq (1H, 4.92+6.26+5.44+7.24), 1.47m+1.25m (2H), 1.3m (4H), 1.01d (3H, 7Hz), 0.91t (3H, 7Hz)  
<sup>13</sup>C (77): 41.51, 35.18 (CH), 34.55, 29.07, 22.74, 18.76, 14.00

#### *Synthesis of BuCH(CN)COOMe*

NaOMe (5.0 g) was dissolved in dry methanol (50 mL) before ethyl cyanoacetate (10 mL) was added and stirred for 1 hr at room temperature to give a pale yellow solution.

Then 1-bromobutane (10 mL) was added via pipette and the reaction heated to 60°C for 4 hrs and then cooled to room temperature and allowed to settle. The red mixture is decanted off any solids and concentrated in vacuo to give a large quantity of solids. The mixture was extracted with 3x 100 mL PET and the extracts concentrated in vacuo. The remaining red liquid is vacuum transferred at 40 mbar and ~300°C to give 9.7g of a colourless clear liquid (159 mmol, 74%). NMR shows a mixture of Bu<sub>2</sub>C(CN)COOMe, BuCH(CN)COOMe and CH<sub>2</sub>(CN)COOMe along with some Et ester and (maybe) R<sub>2</sub>C(COOMe)<sub>2</sub> (R=Bu or H) from nitrile alcoholysis. The product was repeatedly partially distilled through a Vigreux column at 100mbar and then 40mbar to yield 1.84g of a clean middle fraction (80% BuCH(CN)COOMe, 11.86mmol).

#### *Synthesis of (2-MeHexyl)BuCHCN*

This fraction is dissolved in 5ml dry MeOH and 665mg NaOMe (12.3 mmol) is added. After 1hr, 2.51g of the 86w% 2-Me-HexBr (12.0mmol) is added and heated to 60C for 5hrs. The solvent is removed by rotary evaporation and the residue is extracted with pentane. The pentane extract are passed through MgSO<sub>4</sub> and the solvent removed under vacuum (40mbar, 50C) to give 2.5g of a colourless oil (for M=253.39: 9.9mmol or 84%).

Decarboxylation: 2.45g of the product (9.7mmol) in 15ml DMSO with 1.35g LiCl and 0.5ml water are heated to 155C overnight. 30ml water and 30ml pentane are added. The bottom aq phase is taken off with a pipette and the org phase is washed with 20ml water four times. The final organic phase is filtered through MgSO<sub>4</sub>, the solvent removed under vacuum and the residue is vacuum transferred at high vacuum (0.03mbar) at about 100C to give 831mg (92w%, 765mg, M=195.35, 3.9mmol (40%) + 0.6mmol ROH).

NMR of first fraction in CDCl<sub>3</sub> shows 92w% product (rest 2-MeHexylOH).

#### *Synthesis of (2-MeHex)BuCHCHO*

750mg (3.9mmol+0.25 ROH) (2-MeHexyl)BuCHCN are dissolved in dry hexane (15ml) and cooled to -70C (iPrOH/LN<sub>2</sub> bath). Then 5.6ml 1M <sup>i</sup>Bu<sub>2</sub>AlH in hexane (d=0.701, 3.95g, 5.6mmol) is added via syringe over 40min and left stirring at -70C for 2hrs followed by slow warming to 0C. After 30min at 0C, 8ml of cold 6% HCl (of 5ml conc HCl in 20ml water) is added along with 20ml Et<sub>2</sub>O. The aq phase is removed and the organic phase washed with 17ml 6% HCl, dried over MgSO<sub>4</sub> and the solvent is removed under vacuum. The residue is vacuum transferred at high vacuum at about 100C into an ice-water cooled flask to give 600mg of a colourless liquid (96w% product, about 6mol% ROH, rest good by NMR, for (MeHex)BuCHCHO, M=198.35, 2.9mmol, 74%).

#### *Synthesis of mixture of A, A', B and B'*

The product is transferred into a Schlenk tube with 3ml of dry THF, degassed and cooled in an ice bath, about 11ml of a red Ph<sub>3</sub>P=CHBu solution in THF (prepared from 140mg of NaH (M=24, 5.8mmol) and 2.41g of Ph<sub>3</sub>PCH<sub>2</sub>Bu Br (M=413, 5.8mmol) in 14.8g THF) is added slowly until

the red colour does not disappear anymore. The bath is removed and stirred for 1hr. Solvent removal in vacuo, extraction with pentane, solvent removal and two high vacuum transfers at about 300C yield 538mg of clean BuCHMeCH<sub>2</sub>CHBuCH=CHBu (2.13mmol, 74%) as a nearly 1:1 mixture of diastereomers of cis and trans: 4.4(1)% (SS/RR)-trans (A), 44.0(1.2)% (RS/SR)-cis (B), 4.8(3)% (SR/RS)-trans (A') and 46.8(1.2)% (SS/RR)-cis (B') with chemical shifts identical to those reported for the hexene trimers.

#### Synthesis of a mixture of L and M:

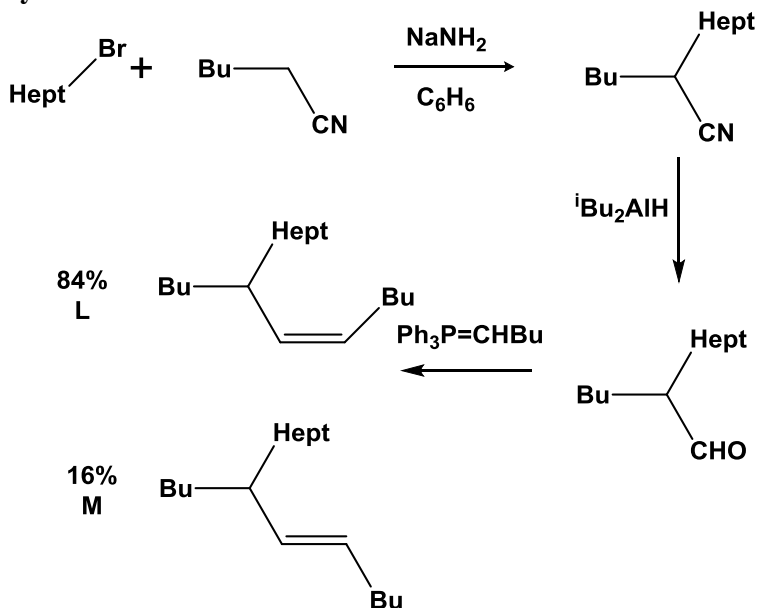


Figure S3. Synthesis of mixture of L and M

#### Synthesis of BuHeptCHCN

[G. Newberry, W. Webster, *J. Chem. Soc.*, 738 (1947)]

Hexanenitrile (2.1g, 21.6mmol) are combined with 1-bromoheptane (M=179.10, d=1.14, 3.5ml, 4.11g, 22.9mmol) and dry benzene (8.4g) and an addition Schlenk tube with solid  $\text{NaNH}_2$  (M=39.01, 940mg, 24.1mmol) is attached. After heating the mixture to 80 °C with stirring the  $\text{NaNH}_2$  is tapped in in small portions so that no excessive heat is produced. Stirring at 80 °C is continued for 1hr with pouring of the slurry into the addition tube to ensure complete addition and is then left at RT overnight. Then water (3ml) is carefully added. The organic phase is taken off, washed with water and combined with further  $\text{Et}_2\text{O}$  extractions of the aqueous phase. The organic phase is dried with  $\text{MgSO}_4$ , rotavapped down and vacuum transferred (high vac, low setting of hot heat gun) to give 3.12g of a colourless liquid (91.6w% BuHepCHCN, M=195.35, 2.86g, 14.6mmol, 68%; 5.5w% HepBr, 1.0mmol; 2.9w% PeCN, 0.9mmol).

NMR neat:

$^1\text{H}$  (lowest Me at 0.787): 2.39quint (1H, J=7), 1.4m (6H), 1.2m (12H), 0.815t (3H, J=7.1), 0.787t (3H, J=7.1)

$^{13}\text{C}$  (lowest Me at 13.93): 121.45, 32.72, 32.41, 32.11, 31.71, 29.60, 29.48, 29.44, 27.49, 22.90, 22.53, 14.15, 13.93

#### Synthesis of BuHeptCHCHO

The nitrile from above (14.6mmol) is dissolved in dry hexane (50ml) and cooled to -70 °C. Then 22ml 1M  $i\text{Bu}_2\text{AlH}$  in heptane (d=0.731, 15.64g, 21.4mmol) is added via septum over 20min while keeping below -50 °C and left stirring at -50 to -70 °C for 30min followed by slow warming to 0 °C. After 30min at 0 °C (2hrs after end of addition), 80ml  $\text{Et}_2\text{O}$  followed by 30ml

of cold 6% HCl is added drop wise over 15min. The aqueous phase is removed and the organic phase washed with 60ml 6% HCl, dried over MgSO<sub>4</sub> and rotavapped down. The residue is vacuum transferred at high vacuum/low heat gun to give 2.20g colourless liquid (99.5w% product, rest Et<sub>2</sub>O, M=198.35, 11.0mmol, 76%).

NMR in CDCl<sub>3</sub>:

<sup>1</sup>H (7.27): 9.53d (1H, J=3.16), 2.20m (1H), 1.60m (2H), 1.41m (2H), 1.2-1.3 (14H), 0.873t (3H, J=6.4), 0.855t (3H, J=6.7)

<sup>13</sup>C (77.00): 205.51 (CHO), 51.92 (CH), 31.72, 29.62, 29.20, 29.05, 28.88, 28.56, 27.04, 22.71, 22.57, 13.99, 13.80

#### *Synthesis of BuHeptCHCH=CHBu (L+M)*

Ph<sub>3</sub>PCH<sub>2</sub>Bu Br (4.50 g, M=413, 10.9mmol, prepared from Ph<sub>3</sub>P and pentyl bromide) and NaH (M=24.00, 265mg, 11.0mmol) are weighted out into a Schlenk tube. Then 40ml of dry THF is added and stirred for 4d. Then the neat BuHeptCHCHO (11.0 mmol) is added dropwise within 10min while stirring. The solution becomes warm and eventually colourless. The colourless solution is decanted after settling. Solvent removal in vacuo after 1hr, extraction with pentane, solvent removal and two high vacuum transfers at about 300C yielding 1.5 containing some aldehyde and Ph<sub>3</sub>P.

NMR shows excess aldehyde of about 0.75mmol. 425mg Ph<sub>3</sub>PCH<sub>2</sub>Bu Br (M=413, 1.03mmol) and 27mg NaH (M=24.00, 1.13mmol) are weighted out into a Schlenk tube, mixed with 5ml of THF and heated to 60 °C for 6hrs to give an orange suspension. The mixture is cooled to 0 °C and then the mixture from above is added and washed in with some dry Et<sub>2</sub>O. This time, the orange colour does not disappear and the mixture was stirred overnight and worked up as above.

Fractional vacuum transfer gives 537mg of a clean middle fraction (M=252.485, 2.13mmol, 19%).

s=3.9% in CDCl<sub>3</sub>(TMS):

<sup>1</sup>H: 84% cis: 5.356dtd (1H, J=10.9+7.3+0.9 Hz), 5.012ddt (1H, 10.9+10.0+1.6 Hz), 2.260m (1H); 16% trans: 5.303dtd (1H, 15.3+6.9+0.4 Hz), 5.079ddt (1H, 15.3+8.7+0.7 Hz), 1.843m (1H); cis+trans: 2.0m (2H), 1.1-1.5 (24H), 0.9m (9H)

<sup>13</sup>C: 84% cis: 135.188, 129.485, 37.128, 36.029, 35.727, 32.194, 31.962, 29.903, 29.644, 29.406, 27.476, 27.421, 22.958, 22.721, 22.460, 14.142, 14.126, 14.034

16% trans: 135.126, 129.959, 42.808, 35.619, 35.321, 32.319, 31.983, 31.952, 29.785, 29.564, 29.395, 27.302, 22.860, 22.72, 22.163, 14.151, 14.13, 13.961

s=42%:

<sup>1</sup>H: 84% cis: 5.354dtd (1H), 5.004ddt (1H), 2.274m (1H); 16% trans: 5.305dtd (1H), 5.076ddt (1H), 1.853m (1H); cis+trans: 2.0m (2H), 1.1-1.5 (24H), 0.9m (9H)

<sup>13</sup>C: 84% cis: 135.235, 129.640, 37.354, 36.298, 35.996, 32.402, 32.198, 30.135, 29.860, 29.646, 27.670, 27.647, 23.143, 22.917, 22.632, 14.206, 14.192, 14.104

16% trans: 135.240, 130.150, 43.095, 35.879, 35.581, 32.526, 32.196, 32.184, 30.013, 29.784, 29.632, 27.530, 32.042, 22.917, 22.351, 14.214, 14.198, 14.023

Neat (TMS) (s=100%):

<sup>1</sup>H: 84% cis: 5.343dtd (1H), 4.987ddt (1H), 2.29m (1H); 16% trans: 5.302dtd (1H), 5.067ddt (1H), 1.86m (1H); cis+trans: 2.0m (2H), 1.1-1.5 (24H), 0.9m (9H)

<sup>13</sup>C: 84% cis: 135.190, 129.748, 37.536, 36.552, 36.248, 32.578, 32.408, 30.337, 30.036, 29.863, 27.838, 27.828, 23.297, 23.089, 22.765, 14.266, 14.257, 14.171

16% trans: 135.293, 130.284, 43.344, 36.113, 35.813, 32.702, 32.391, 32.375, 30.207, 29.964, 29.846, 27.723, 23.191, 23.089, 22.501, 14.271, 14.264, 14.080

## Assignment of regioisomers

A/A' and B/B':

NMR shift differences between diastereomers are compared to those of a related compound of known regiochemistry [18]. In the case of B', isolated  $^1\text{H}$  NMR signals allow the observation of a key-NOE effect to confirm this assignment.

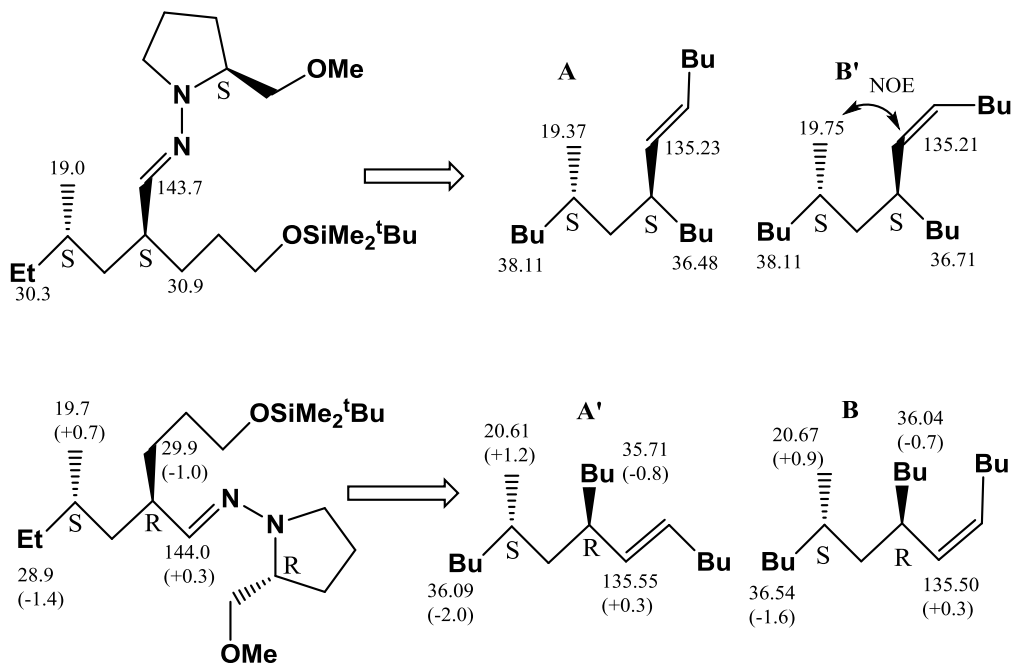


Figure S4. NMR assignment of A/A' and B/B' based on related compounds with known stereochemistry.

D and D':

These can be assigned in a similar way and is confirmed by a NOE interaction:

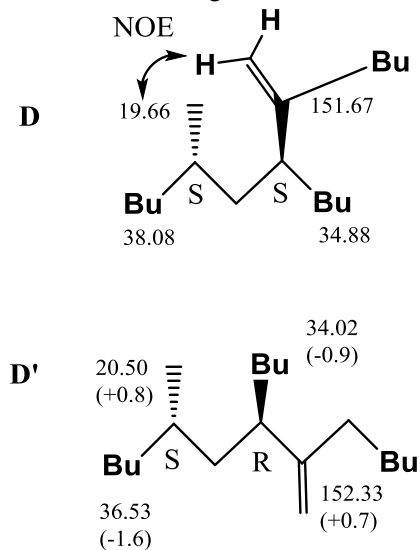


Figure S5. NMR assignment of D/D' based on related compounds (Fig S4) and NOE signal.



E and E':

Chem3D molecular mechanics optimisation of all possible conformers gives the following lowest energy conformer the syn and anti conformers for the three bonds between (red)  $^{13}\text{C}$  labels  $\text{C}_b$  and  $\text{C}_c$  (observed  $J_{bc}$ ):

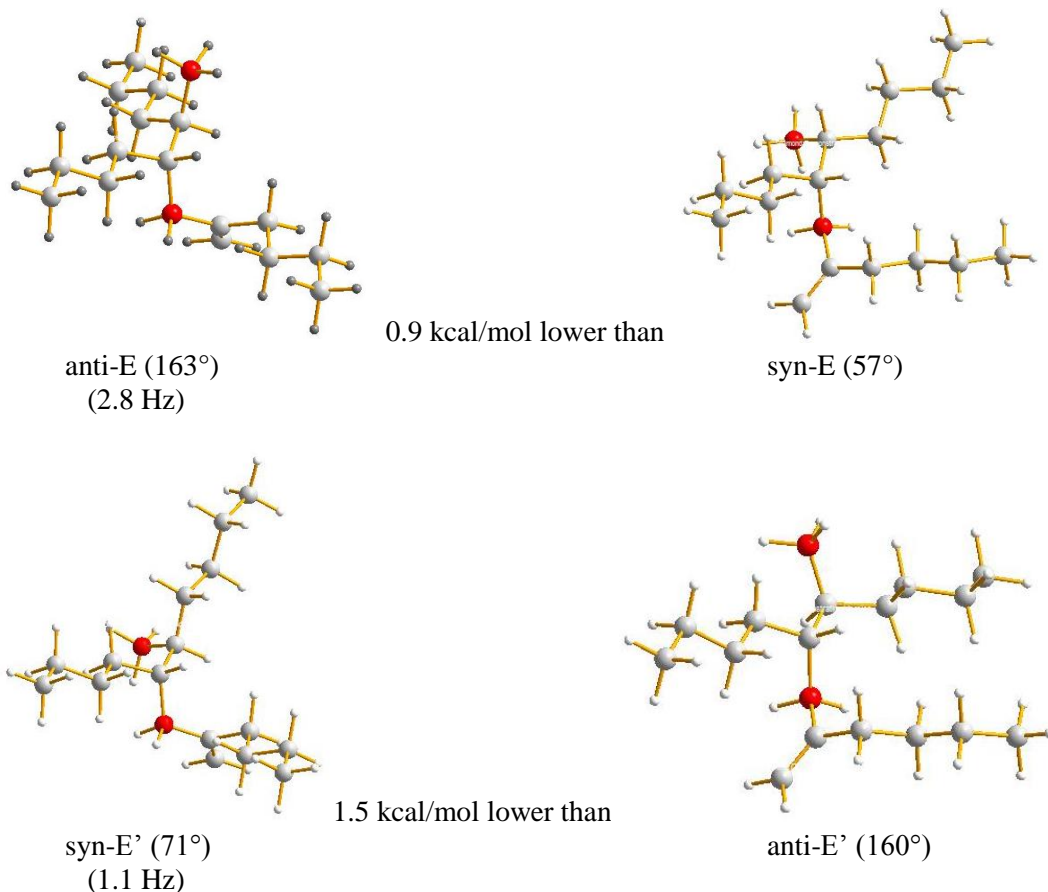


Figure S6. Chem3D optimised conformers of E/E' for NMR assignment using the torsion angle and J coupling between the C atoms labelled in red.

Assignment of regioisomers F/F' and G/G':

Chem3D molecular mechanics optimisation (Bu at olefin reduced to Me) of all possible conformers gives the following lowest energy conformer the syn and anti conformers for the three bonds between  $^{13}\text{C}$  labels  $\text{C}_b$  and  $\text{C}_c$  (observed  $J_{bc}$ ):

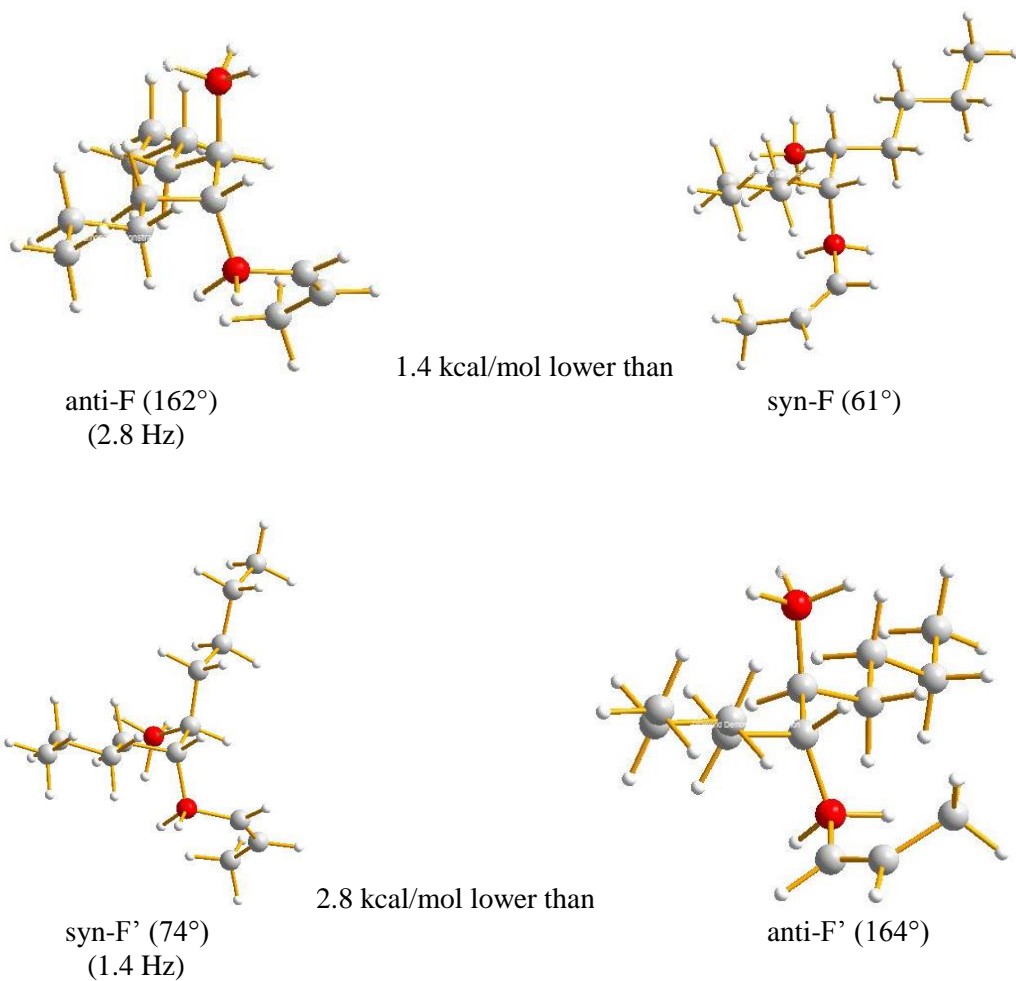
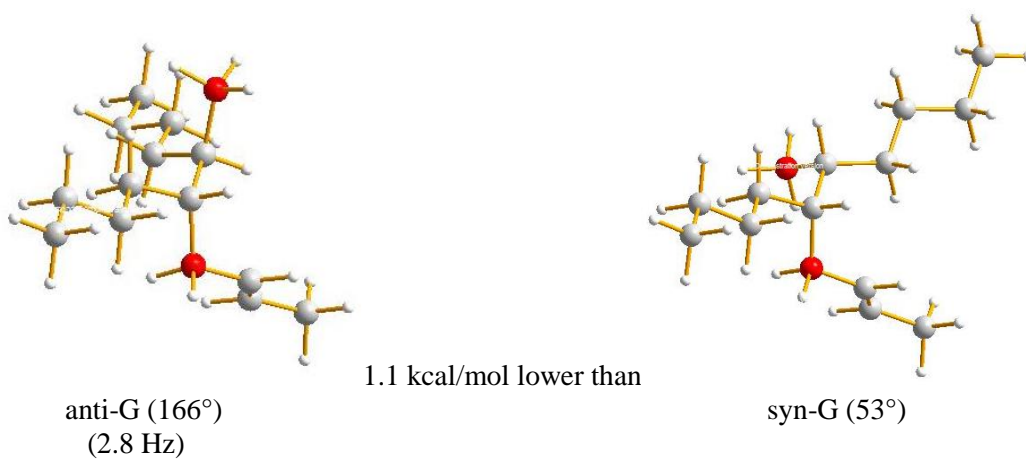


Figure S7. Chem3D optimised conformers of F/F' for NMR assignment using the torsion angle and J coupling between the C atoms labelled in red.



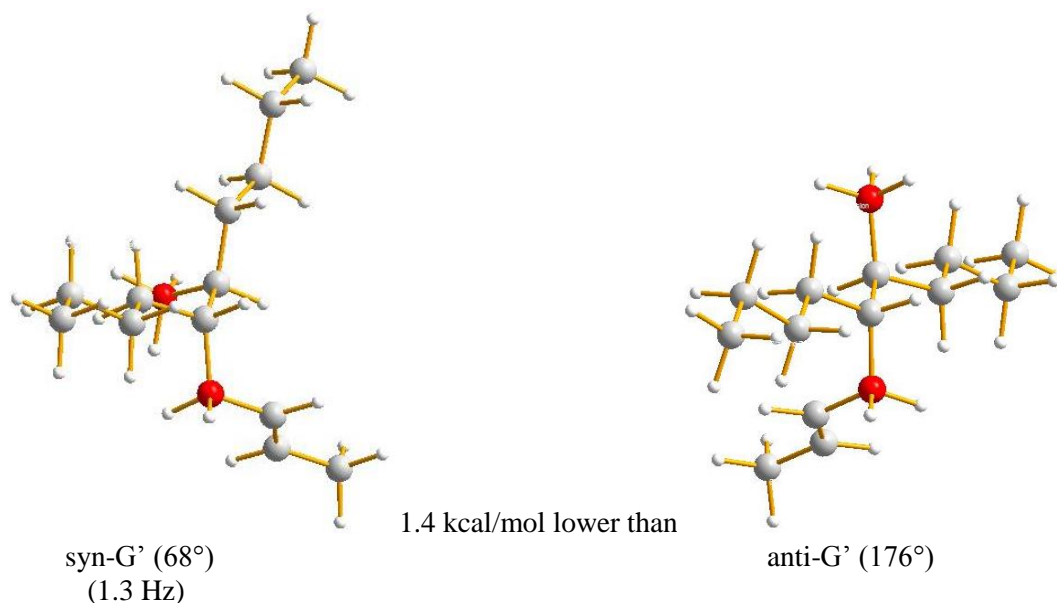


Figure S8. Chem3D optimised conformers of G/G' for NMR assignment using the torsion angle and J coupling between the C atoms labelled in red.

In all cases where the anti conformer dominates, the J value is around 2.8 Hz high and in those cases with dominating syn conformer around 1.2 Hz are found as expected according to the Karplus relationship for vicinal coupling.

**IUPAC names of 1-hexene trimers** (racemates for chiral compounds):

- A: (5E,7S,9S)-7-butyl-9-methyltridec-5-ene
- A': (5E,7R,9S)-7-butyl-9-methyltridec-5-ene
- B: (5Z,7S,9S)-7-butyl-9-methyltridec-5-ene
- B': (5Z,7R,9S)-7-butyl-9-methyltridec-5-ene
- D: (6S,8S)-6-butyl-8-methyl-5-methylidenedodecane
- D': (6R,8S)-6-butyl-8-methyl-5-methylidenedodecane
- E: (5R,6S)-6-butyl-5-methyl-8-methylidenedodecane
- E': (5S,6S)-6-butyl-5-methyl-8-methylidenedodecane
- F: (5E,8S,9R)-8-butyl-9-methyltridec-5-ene
- F': (5E,8R,9R)-8-butyl-9-methyltridec-5-ene
- G: (5Z,8S,9R)-8-butyl-9-methyltridec-5-ene
- G': (5Z,8S,9S)-8-butyl-9-methyltridec-5-ene
- H: 6-butyl-5-methylidenetridecane
- I: (5Z)-8-butyltetradec-5-ene
- K: (5E)-8-butyltetradec-5-ene
- L: (5Z)-7-butyltetradec-5-ene and (5Z)-7-butyltetradec-5-ene
- M: (5E)-7-butyltetradec-5-ene and (5Z)-7-butyltetradec-5-ene

## GCMS Supporting Information

The trimer products were also analysed extensively using GCMS analysis which was performed on two different spectrometers fitted with different columns. The first was an Agilent 7890B with Agilent 5977A MSD and FID detectors. This spectrometer was equipped with a DB-FFAP column 30 m in length, with a diameter of 0.250 mm and a 0.25  $\mu\text{m}$  film thickness. The second was an Agilent 7890A with Agilent 5975C MSD and FID detectors. This spectrometer was equipped with a HP-5 column 30 m in length, with a diameter of 0.320 mm and a 0.25  $\mu\text{m}$  film thickness. A ramp rate of 3  $^{\circ}\text{C}$  per minute was used from 40 to 350  $^{\circ}\text{C}$  in both cases.

An example for a trimer mix produced by 1b is shown in Figure S9. Despite all having the same molecular mass the different regioisomers can be separated to some extent with the use of a 30 m column and 3 $^{\circ}\text{C}$  per minute temperature increases. The use of two columns of different specification resulted in a slightly improved picture and facilitated identification. The FID integrations of the products were correlated with those calculated from  $^{13}\text{C}$  NMR analysis in order to assign the major peaks observed.

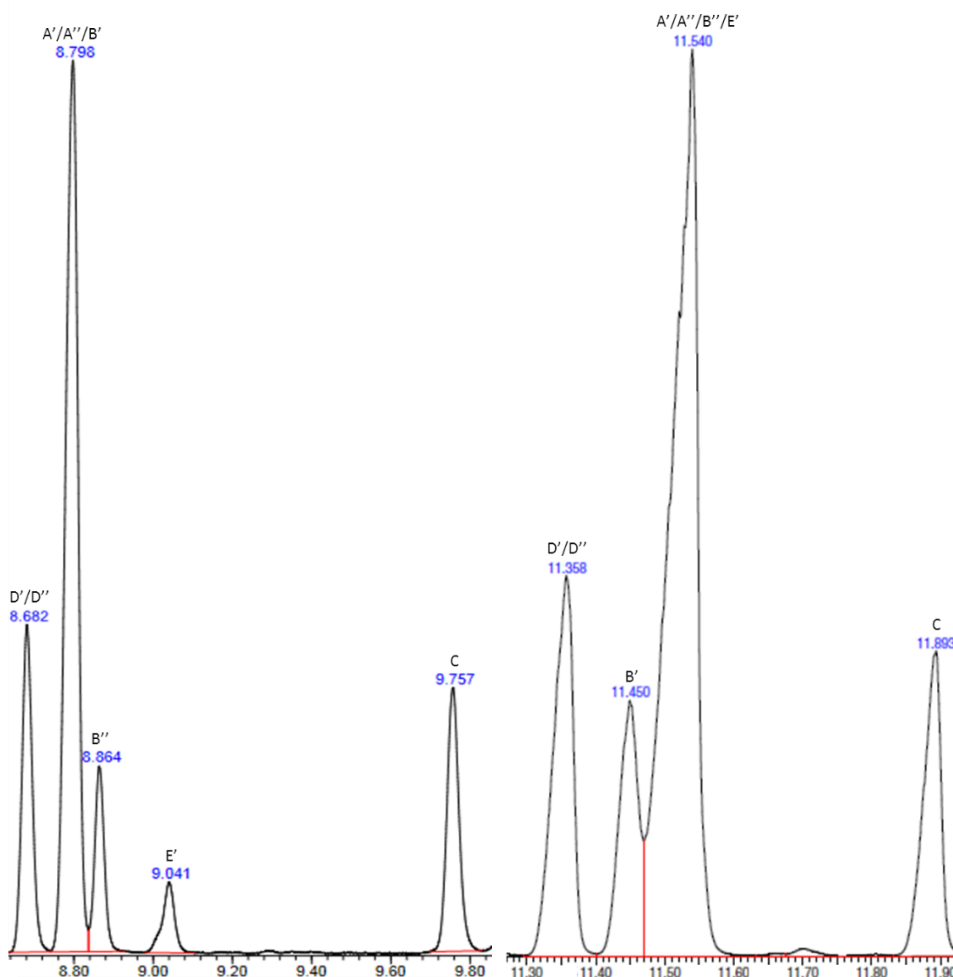


Figure S9. The FID spectra in the region representing the major isomers of 1-hexene trimers. The spectra on the left was collected using the DB-FFAP column, the spectra on the right was collected using the HP-5 column. (retention time in minutes, arbitrary intensity)

Four small peaks were observed at retention times for both columns but due to the error inherent in the correlation they could not be accurately assigned. Similarly, it cannot be assumed that none

of the minor isomers are contained within the peaks shown. Due to the significant overlap of peaks the relative abundance of products was routinely calculated based on  $^{13}\text{C}$  NMR integration. For quantification by GC-MS, the response factor of the GC-FID integration relative to added biphenyl was determined by calibration with 1-octene, 1-decene, dodecane, 1-hexadecene and isolated hexene and octene trimer. The response factor for isomers was assumed to be identical.

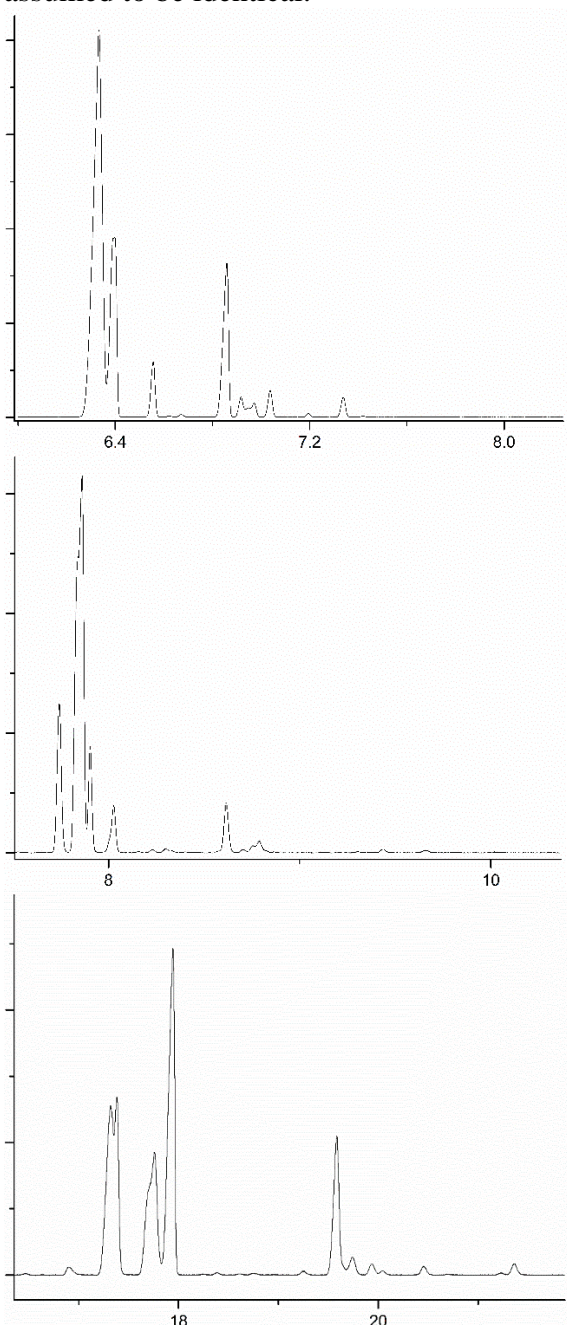


Figure S10. The FID spectra in the region of the 1-pentene, 1-hexene and 1-octene trimers (top to bottom) with the same GC programme. (retention time in minutes, arbitrary intensity)

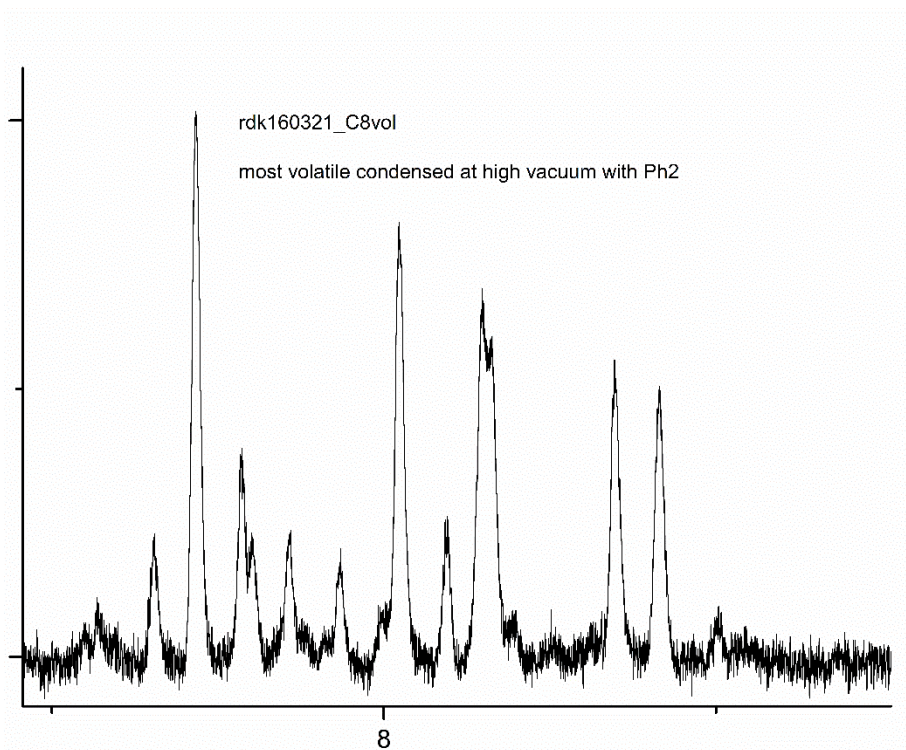


Figure S11. 1-Octene dimer region in GC-MS. (retention time in minutes, arbitrary intensity)

### Concentration dependence of NMR signals:

Concentration dependence of the trimer shifts was measured in the range of high dilution (few %) to neat. The concentration was determined by weighing the trimer and solvent as well as by the concentration dependence of the residual  $\text{CHCl}_3$  and  $\text{C}_6\text{D}_5\text{H}$  signal against internal TMS (<1%). The later was found to be linear when the concentration was expressed by a “surface fraction”  $s$  as defined below. Using this  $s$ , we also found identical dependence of the  $\text{CHCl}_3$  or  $\text{C}_6\text{D}_6$  solvent shift for solutions of pentene and hexene trimers further supporting this concentration measure as suitable for this study.

$$s = x/[x + \alpha(1-x)] \quad \text{with } x = \text{mol fraction} = M_{\text{CDCl}_3}x_{\text{trimer}}/m_{\text{CDCl}_3}/M_{\text{trimer}},$$

$$\alpha = [M_{\text{CDCl}_3}x_{\text{trimer}}/d_{\text{CDCl}_3}/M_{\text{trimer}}]^{2/3} = 0.3970$$

$$\text{or } s = 1/[1 + [M_{\text{trimer}}x_{\text{trimer}}/d_{\text{L}}^2/M_{\text{L}}]^{1/3} m_{\text{L}}/m_{\text{trimer}}]$$

$$= 1/[1 + \beta m_{\text{L}}/m_{\text{trimer}}] \quad \text{with } \beta = [M_{\text{trimer}}x_{\text{trimer}}/d_{\text{L}}^2/M_{\text{L}}]^{1/3}$$

$\beta$  for pentene trimers:  $\text{CDCl}_3$ : 0.6831,  $\text{C}_6\text{D}_6$ : 1.1850

hexene trimers:  $\text{CDCl}_3$ : 0.8341,  $\text{C}_6\text{D}_6$ : 1.2744

octene trimers:  $\text{CDCl}_3$ : 0.9266,  $\text{C}_6\text{D}_6$ : 1.4156

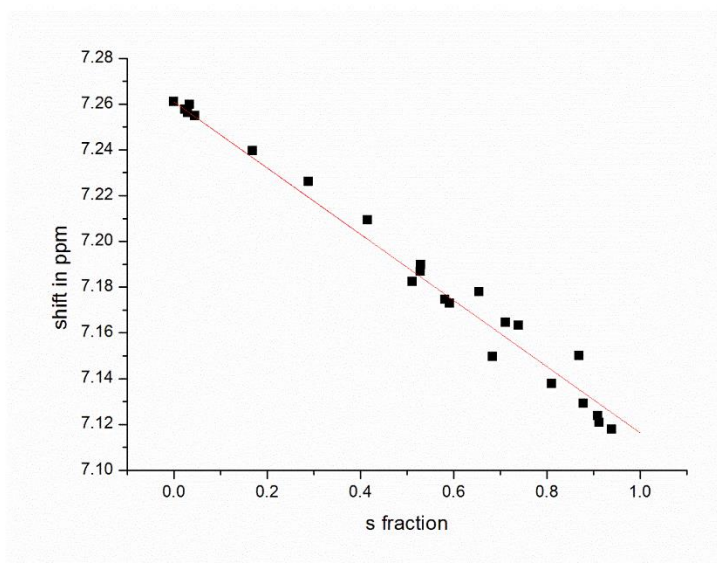


Figure S12. Shift of residual  $\text{CHCl}_3$  in  $\text{CDCl}_3$ :  $\delta = 7.261(1) - 0.1451(24) s$

Shift of  $\text{C}_6\text{D}_5\text{H}$ :  $\delta = 7.1548(12) (1-s) + 7.235(3) s - 0.06(1) s(1-s)$

(exp data from reliable concentration by weight, for both pentene and hexene trimers)

$s$  can be converted back to  $x = \alpha/[\alpha - 1 + 1/s]$

Use of the  $s$  fraction gives more linear relationships for the subsequent data.

These relationships can be used to calculate the concentration of any solution with TMS as standard.

Use of  $^{13}\text{C}$  data of the trimer for the determination of concentration:  
 The olefinic signals around 135ppm show different concentration dependence and the shift difference  $\Delta$  between the two largest signals (furthest left **B** and right **A** at low concentration) can be used:

$$\Delta = 0.4695(12) - 0.2225(20) s \text{ or } s = [0.4695 - \Delta]/0.2225$$

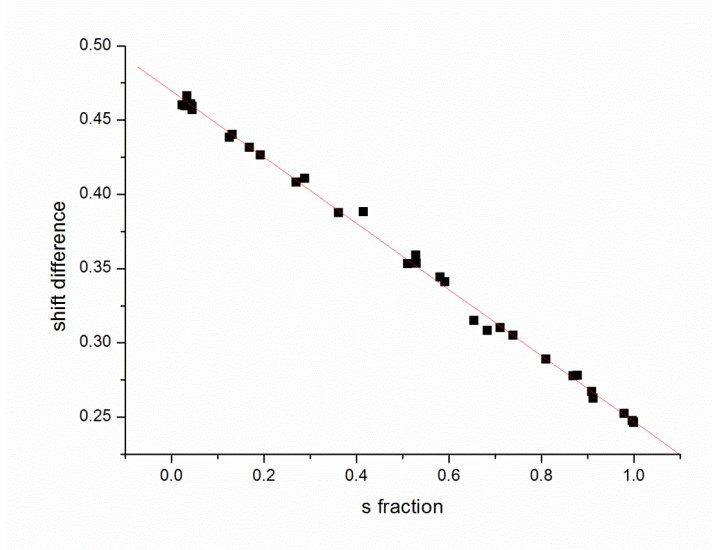


Figure S13. Dependence of  $\Delta$  on  $s$ .

The absolute shift of the largest signal (furthest upfield at low concentration):

$$\delta = 135.034(1) (1-s) + 135.238(2) s + 0.170(7) s(1-s)$$

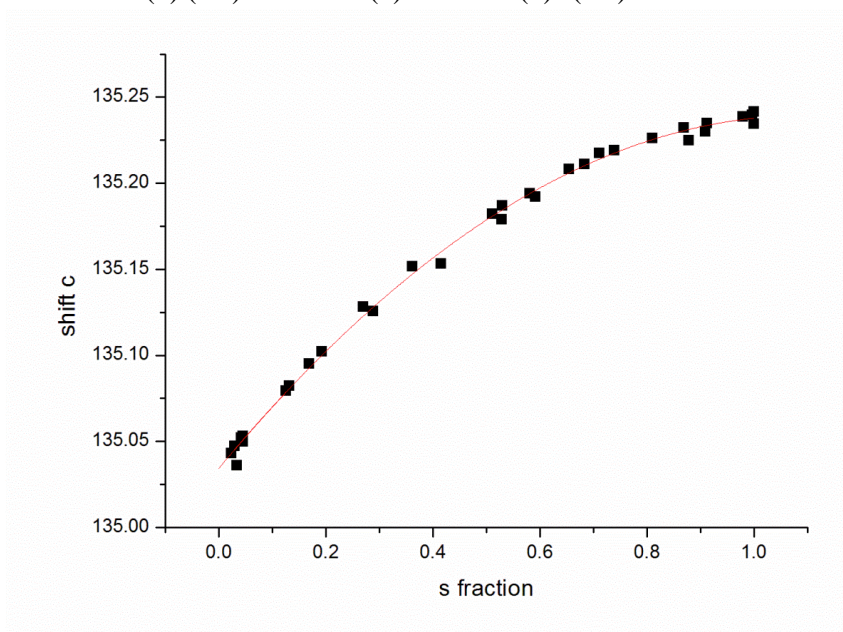


Figure S14. Dependence of the absolute shift of the furthest upfield  $^{13}\text{C}$  signal of the 1-hexene trimer **A** on  $s$ .



Thus, concentration (first as  $s$ , then converted to  $x$ ) and shift correction ( $\delta_{\text{calcd}} - \delta_{\text{obs}}$ ) can be determined without the presence of TMS!

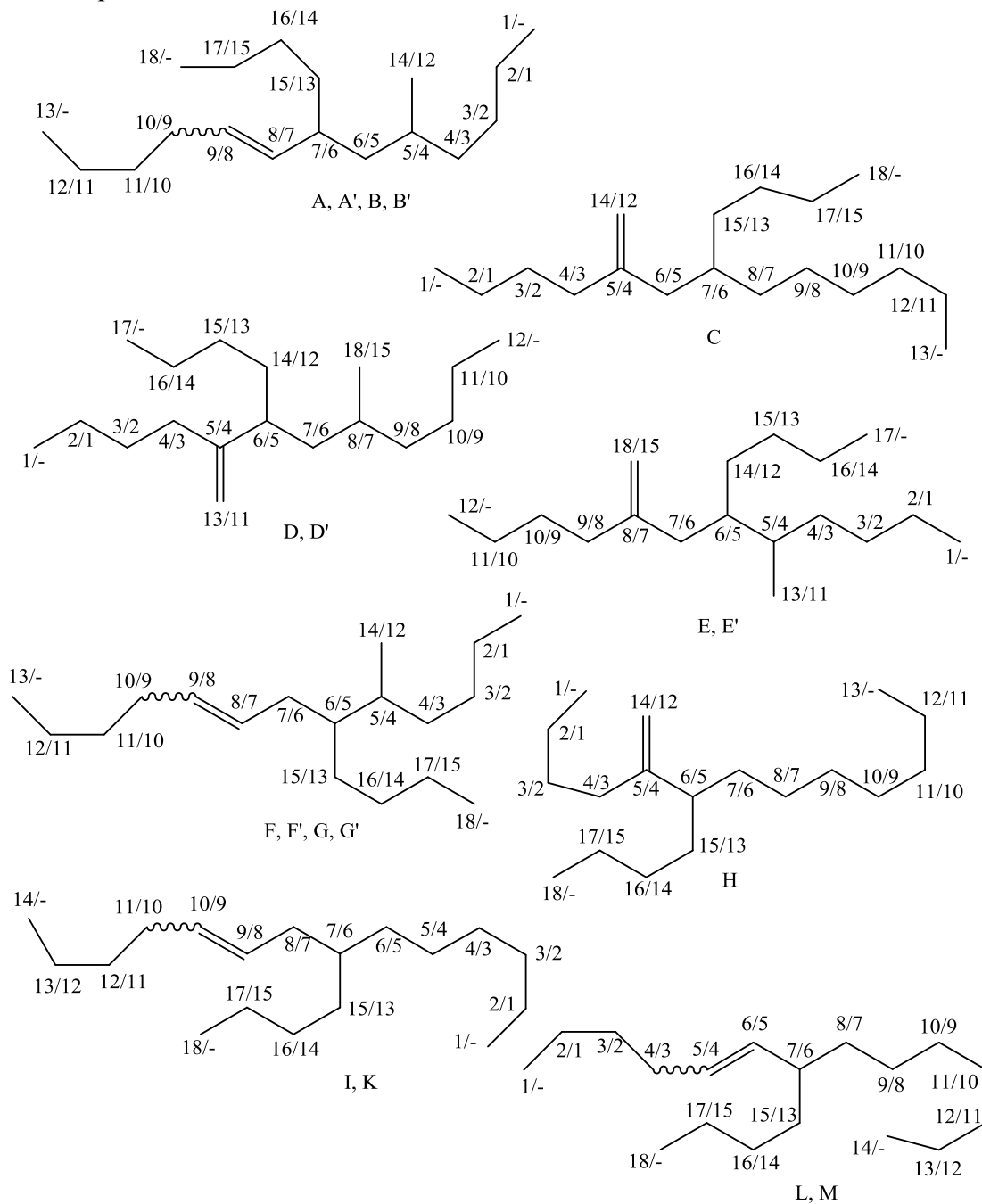
All peaks can be fitted to the following equation:

$$\delta = \delta_0 (1-s) + \delta_{\text{neat}} s + \lambda s (1-s) = \delta_0 + \Delta s + \lambda s (1-s)$$

( $\delta_0$  shift at infinite dilution in  $\text{CDCl}_3$  and  $\Delta = \delta_{\text{neat}} - \delta_0$ )

**Figure S15. Numbering Scheme for NMR assignment:**

The observed shifts are given in separate Excel files using the following numbering scheme for hexene / pentene trimers:



## Detailed distribution of isomers according to quantitative $^{13}\text{C}$ NMR

Table S1. The regioisomers produced across the catalyst range – two values given for diastereomers X + X'.

Catalyst	Regioisomer Abundance (%)											
	A	B	C	D	E	F	G	H	I	K	L	M
1a	28.4+	14.2+	11.8	13.9+	2.9+	1.3+	0.60+	0.36	0.20	1.20	0.36	0.65
	11.5	8.2		2.6	0.7	0.7	0.34					
C5	29.5+	14.0+	13.1	12.5+	3.0+	1.35+	0.58+	0.35	0.29	1.34	0.37	0.84
	11.1	7.7		2.3	0.8	0.53	0.43					
1b	28.7+	11.7+	15.5	13.2+	3.0+	1.3+	0.5+	0.6	0.2	1.5	0.4	1.4
	9.8	7.5		2.4	0.7	0.6	0.3					
C5	31.2+	11.9+	14.2	12.5+	3.0+	1.23+	0.55+	0.34	0.31	1.50	0.37	1.13
	9.9	7.8		2.3	0.7	0.61	0.42					
C8	28.7+	12.9+	13.2	13.7+	3.2+	1.05+	0.36+	0.41	0.31	1.18	0.52	0.92
	10.8	8.5		2.7	0.7	0.52	0.35					
1c	36.2+	8.4+	3.0	17.0+	7.2+	1.95+	1.00+	0.26	0.17	0.72	0.28	0.74
	10.7	6.9		2.7	1.1	1.19	0.53					
1d	19.2+	19.8+	1.6	17.9+	8.1+	1.7+	0.4+	0.1	0	0.4	0	0.3
	17.7	9.0		1.9	1.0	0.5	0.3					

Table S2. The regioisomer abundance (%) of 1- $^{13}\text{C}$ -1-hexene produced by **1b**.

A	B	C	D	E	F	G	H	I	K	L	M
A'	B'		D'	E'	F'	G'					
31.7	12.7	13.2	13.6	2.8	0.80	0.44	0.46	0.17	0.85	0.39	0.50
10.0	8.0		2.5	0.70	0.49	0.25					

**Increments obtained for the difference in shift of corresponding signals in hexene and pentene trimers:**

Average increments (followed by standard deviation and standard error) for C6-C5 (A-E only) ( $\varepsilon^\pi$  means  $\varepsilon$  via a double bond) [value from increments introduced by Grant and Paul [22]:

neat	CDCl3	C6D6	neat	CDCl3	C6D6
$\alpha$ [+9.1]			$\varepsilon$ [+0.1]		
8.790398	8.611813	8.786913	0.04035	0.060657	0.080493
0.043209	0.044879	0.067142	0.017384	0.011798	0.032477
0.00882	0.009161	0.013705	0.00657	0.004459	0.012275
$\beta$ [+9.4]			$\varepsilon\varepsilon$		
9.182926	9.159775	9.180652	0.000764	0.031867	0.078034
0.078793	0.088545	0.089167	0.019153	0.019032	0.023294
0.016083	0.018074	0.018201	0.006384	0.006344	0.007765
$\gamma$ [-2.5]			$\varepsilon\varepsilon^\pi$		
-2.61858	-2.59961	-2.49883	-0.18988	-0.14133	-0.12825
0.12163	0.288874	0.129285	0.016972	0.031055	0.027283
0.024828	0.058966	0.02639	0.008486	0.015528	0.013642
$\delta$ [+0.3]			$\varepsilon^\pi$		
0.183468	0.226278	0.264308	-0.12113	-0.11998	-0.07268
0.064517	0.067679	0.04996	0.047973	0.040969	0.066136
0.015207	0.015952	0.011776	0.023987	0.020485	0.033068
$\delta\varepsilon$ [+0.4]					
0.190298	0.26065	0.27785			
0.044112	0.033435	0.034618			
0.018009	0.01365	0.014133			

**Average increments obtained for the difference in shift of corresponding signals in neat octene and hexene trimers (SD):**

$>\varepsilon$ : -0.03(4) [0]  
 $\varepsilon$ : -0.02(5) [+0.1]  
 $\delta\varepsilon$ : +0.27(6) [+0.4]  
 $\gamma\delta$ : -2.2(5) [-2.2]  
 $\beta\gamma$ : +6.69(6) [+6.9]  
 $\alpha\beta$ : +18.06(2) [+18.5]

The good match of the increments confirms the correct assignment for pentene and octene trimers relative to hexene trimers.