

Electronic Supplementary Information

for

Selective dimerisation of α -olefins using tungsten-based catalysts

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Identification of Dienes

^1H , ^1H -COSY spectrum of a C_{10} fraction enriched in trace products, obtained from an automated distillation of reaction product from a 1-pentene dimerisation with $\text{WCl}_6/\text{PhNH}_2/\text{Et}_3\text{N}/\text{EtAlCl}_2$ (1:2:4:12). The chemical shift of the two doublets at ~ 2.7 ppm is characteristic of a methylene unit between two alkene moieties (diene) and the two doublets at ~ 2.7 ppm show both $^3J_{\text{HH}}$ or $^4J_{\text{HH}}$ cross-peaks with both types of olefinic hydrogens (b,c,d) clearly indicative of diene functionality.

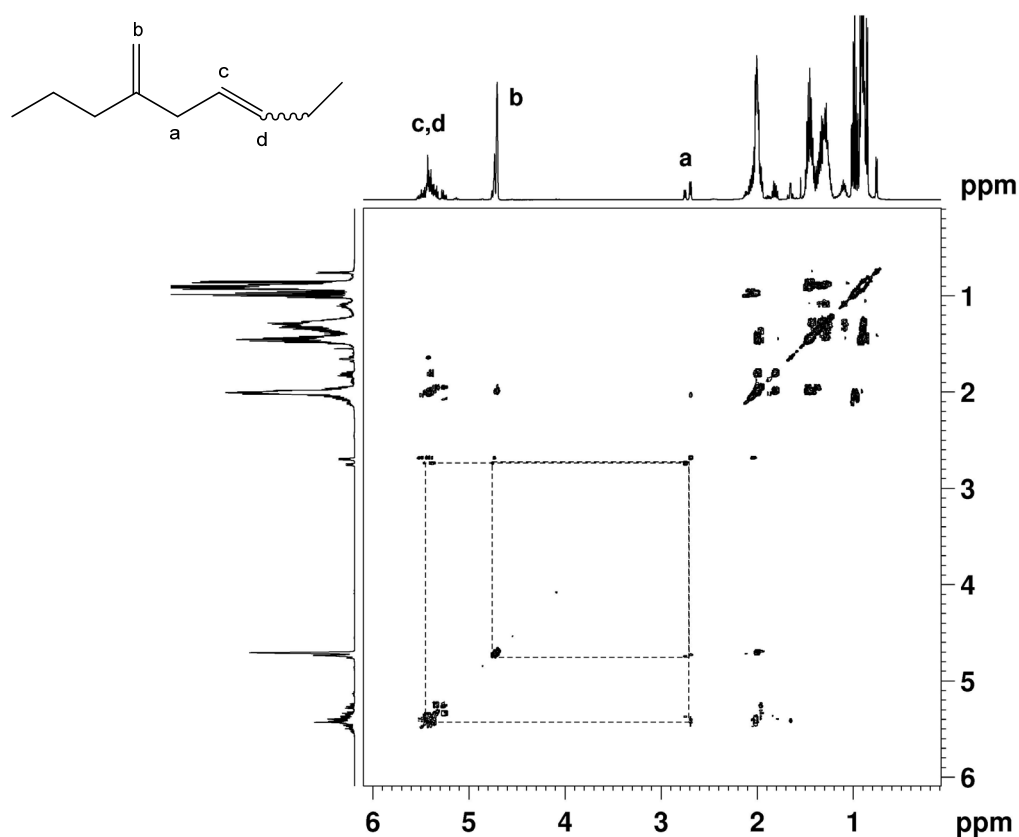


Figure S1. ^1H , ^1H -COSY spectrum of a C_{10} fraction enriched in trace products.

Expanded region of $^1\text{H},^1\text{H}$ -COSY spectrum showing cross-peaks of methylene hydrogens (a) with olefinic hydrogens (c,d). The $^3J_{\text{HH}}$ cross-peak (highlighted by dashed line) of more abundant isomer shows a bigger passive coupling than the cross peak of the less abundant isomer enabling identification of dienes as *trans*- and *cis*-isomers, respectively. The 1.93:1 relative integration ratio measured for the two doublets in the ^1H NMR, now identified as *trans* (relative integration 2) and *cis* (relative integration 1), respectively, allowed subsequent assignment in the GC trace of which peak corresponded to which isomer, the two peaks having a 1.78:1 relative integration in the GC trace of the fraction after distillation.

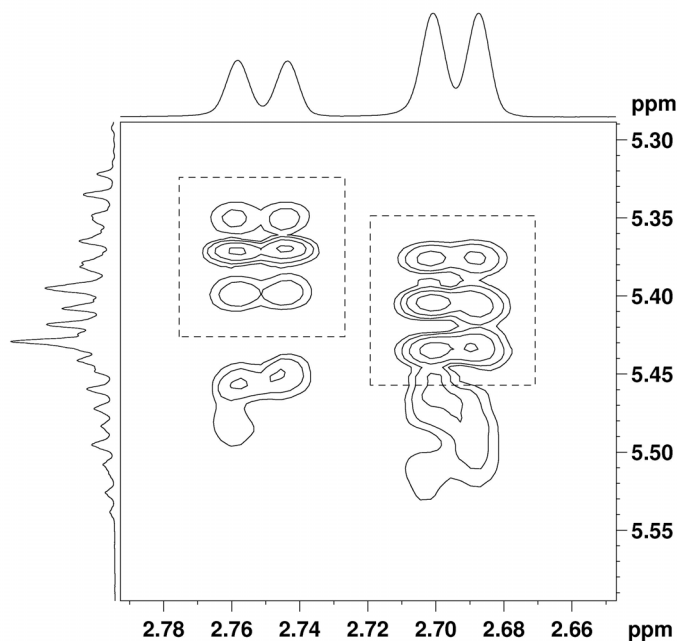


Figure S2. Expansion of Figure S1.

Theoretical metallacyclic mechanism – discounted by experiment

The products expected from a metallacyclic mechanism, and the routes to their formation, are shown in Figure S3 below. Diene formation would result from double β -hydride elimination; alkane formation would occur *via* the resulting tungsten dihydride species. This mechanism is discounted based on the experimental evidence.

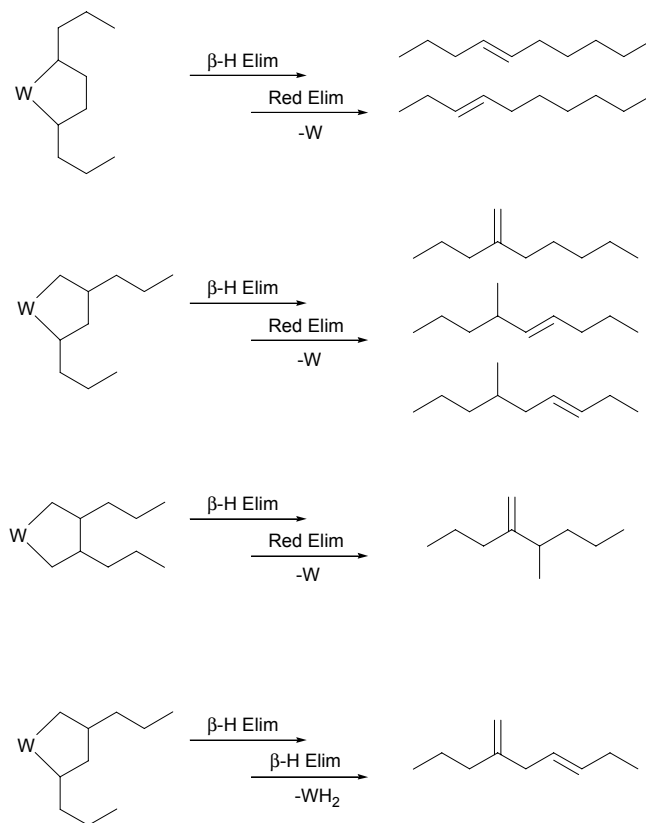


Figure S3. Theoretical metallacyclic mechanism.

Alternative explanation for diene formation *via* intermolecular C-H activation –
discounted by experiment

The intermolecular C-H activation mechanism proposed by Small *et al.*,¹ is not considered viable for this catalyst as it should primarily produce the conjugated diene 2-propyl-1,3-heptadiene, which is not observed. A pathway can be envisaged that would lead to the observed 2-propyl-1,4-heptadiene, however this invokes a 1,3-hydride shift rearrangement of the W-alkenyl. This would be expected to be disfavoured based on computational studies which suggest transition metal bond strengths to decrease in the series $M-C(sp) > M-C(sp^2) > M-C(sp^3)$, thus such a rearrangement would be thermodynamically unfavourable.²

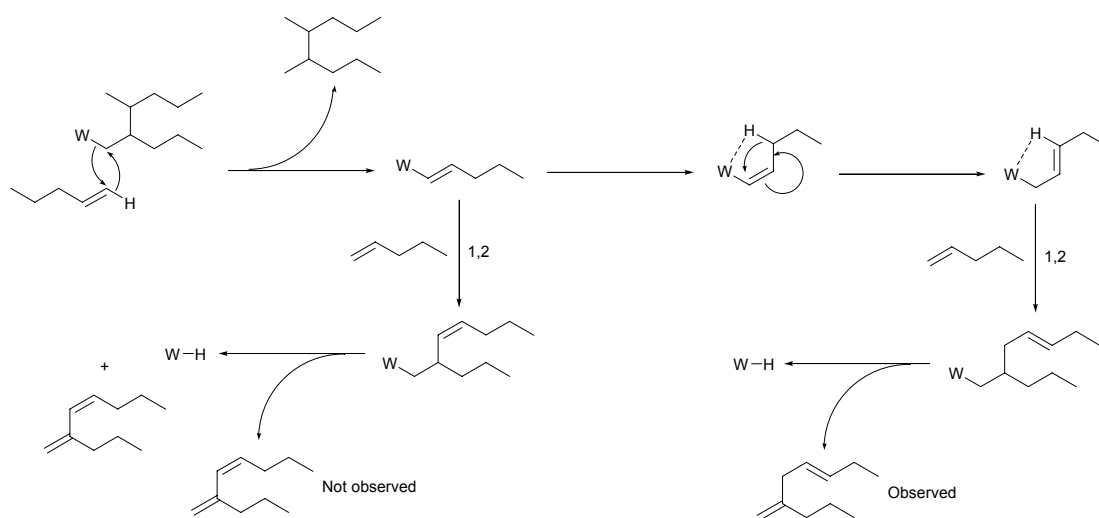


Figure S4. Intermolecular C-H activation route to diene formation.

- 1 B. L. Small, R. Schmidt, *Chem. Eur. J.*, 2004, 10, 1014-1020.
- 2 P. E. M. Siegbahn, *J. Phys. Chem.*, 1995, **99**, 12723-12729.

Experimental

Synthesis of GC-standards

4,5-Dimethyloctane. Prepared according to the literature,³ and identified as the desired alkane by GC-MS, and >95% pure by GC. ¹³C NMR (CDCl₃, 75.46 MHz) δ_C: 37.7 (s, CH), 37.6 (s, CH₂), 36.8 (s, CH), 35.6 (s, CH₂), 21.3 (s, CH₂), 21.2 (s, CH₂), 16.6 (s, CH₃), 14.7 (s, CH₃), 14.6 (s, CH₃), 14.5 (s, CH₃).

4-Methylnonane. A solution of 2-propyl-1-heptene (2 mL) in 50:50 MeOH/EtOH (10 mL) and Pd/C (1.0 g, 5 wt % Degussa type E1002 U/W) was placed in a *s/s* autoclave and mechanically stirred. The vessel was maintained at 50°C and 20 bar H₂ for 24 hours, before cooling and venting. The solution was filtered, the solid washed with EtOH (2 × 10 mL) and the solvent removed *in vacuo*, to leave a colourless oil positively identified as the alkane by GC-MS, and >99.9% pure by GC. ¹H NMR (CDCl₃, 300.06 MHz) δ_H: 1.55-1.30 (m, 10H), 1.28-1.12 (m, 2H), 0.95-1.05 (m, 8H). ¹³C NMR (CDCl₃, 75.46 MHz) δ_C: 40.3 (s, CH₂), 37.9 (s, CH₂), 33.4 (s, CH), 33.1 (s, CH₂), 27.7 (s, CH₂), 23.6 (s, CH₂), 21.0 (s, CH₂), 20.3 (s, CH₃), 15.1 (s, CH₃), 14.8 (s, CH₃).

C₁₀H₂₀ isomers: 2-Methyl-1-bromopentane was prepared from the reaction of 2-methylpentanol and PBr₃ in Et₂O at 0°C.⁴ CuI.PBu₃ was prepared according to the literature.⁵ The methods below are modifications of literature procedures for Wittig synthesis⁶ or cuprate-based couplings.⁷

4-Methyl-1-nonene. Allylmagnesium chloride (20 mL, 40 mmol, 2.0M in THF) was added to a THF (20 mL) suspension of CuI.PBu₃ (1.57 g, 4 mmol) at 0°C under N₂. After stirring for 5 minutes, a THF (20 mL) solution of 2-bromoheptane (6.2 mL, 7.12 g, 40 mmol) was added dropwise and the mixture left to stir and warm to RT overnight. The mixture was carefully quenched with distilled water (250 mL), filtered and extracted with hexanes (5 × 100 mL). The combined organic fractions were dried with MgSO₄, filtered and the solvent removed *in vacuo*. The crude oil obtained was subjected to a short path distillation to leave a pale yellow liquid. This was then subjected to a fractional distillation to yield the product as a colourless liquid (2.86 g, 51%). ¹³C NMR (CDCl₃, 75.46 MHz) δ_C: 137.6 (s, C(R)H=CH₂), 115.4 (s, C(R)H=CH₂), 41.7 (s, CH₂), 36.8 (s, CH₂), 33.0 (s, CH), 32.4 (s, CH₂), 26.8 (s, CH₂), 22.9 (s, CH₂), 19.5 (s, CH₃), 14.2 (s, CH₃).

4-Methyl-2-nonene. A suspension of Mg turnings (6.08 g, 0.25 mol) and one crystal of I₂ in THF (100 mL) was stirred at RT under N₂. 2-Bromoheptane (15.6 mL, 17.80 g, 100 mmol) was added dropwise at a rate that lead to and sustained reflux, after which the mixture was refluxed for 30 minutes, then cooled to 0°C and CuI.PBu₃ (1.96 g, 5.0 mmol) added. 1-Bromo-1-propene (4.3 mL, 6.05 g, 50 mmol) as a solution in THF (50 mL) was then added dropwise and the vessel stirred at 0°C for 30 minutes, before being allowed to warm to RT overnight. The mixture was carefully quenched with distilled water (200 mL), filtered and extracted with hexanes (5 × 100 mL). The combined organic fractions were dried with MgSO₄, filtered and the solvent removed *in vacuo*. The crude oil obtained was subjected to a short path distillation to leave a pale yellow liquid. This was then subjected to a fractional distillation to yield the product as a colourless liquid (2.65 g, 38%). ¹³C NMR (CDCl₃, 75.46 MHz) δ_C: 138.0 (s, *trans*-C(R)H=C(Me)H), 137.7 (s, *cis*-C(R)H=C(Me)H), 122.9 (s, *trans*-C(R)H=C(Me)H), 122.3 (s, *cis*-C(R)H=C(Me)H), 37.9 (s, CH), 37.0 (s, CH), 35.3 (s, CH₂), 33.2 (s, CH₂), 32.7 (s, CH₂), 27.9 (s, CH₂), 27.8 (s, CH₂), 23.1 (s, CH₂), 21.4 (s, CH₃), 21.1 (s, CH₃), 16.7 (s, CH₃), 14.6 (s, CH₃), 14.4 (s, CH₃), 13.1 (s, CH₃).

4-Methyl-3-nonene. In a 3 L, 3-neck round bottom flask (RBF) equipped with magnetic stirrer and reflux condenser under N₂, ⁿBuLi (100 mL, 1.0 mol, 10.0M in hexanes) was added dropwise *via* a pressure equalising dropping funnel (PEDF) to a THF (1000 mL) solution of Ph₃P(ⁿPr)Br (385 g, 1.0 mol) at 0°C. After addition was complete, the solution was allowed to warm to RT briefly then re-cooled to 0°C. A solution of 2-heptanone (154 mL, 125 g, 1.1 mol) in THF (200 mL) was added dropwise *via* PEDF. The mixture was allowed to stir and warm to RT overnight. The reaction was quenched carefully *via* dropwise addition of distilled water (500 mL) from a PEDF. The aqueous layer was then extracted with hexanes (3 × 300 mL), and the combined organic fractions dried over MgSO₄, filtered and the volatiles removed *in vacuo*. The crude oil obtained was subjected to a short path distillation to leave a pale yellow liquid. This was then subjected to a fractional distillation to yield the product as a colourless liquid (88.2 g, 63%). Purity = 98.1% (GC). ¹H NMR (CDCl₃, 300.06 MHz) δ_H: 5.29 (m, 1H), 2.15-1.98 (m, 4H), 1.79 (s, 80% of 3H, CH₃), 1.76 (s, 20% of 3H, CH₃), 1.60-1.14 (m, 6H), 1.06-0.85 (m, 6H). ¹³C NMR (CDCl₃, 75.46 MHz) δ_C: 135.1 (s, *trans*-C(R)H=C(R)H), 135.0 (s, *cis*-C(R)H=C(R)H), 126.9 (s, *trans*-C(R)H=C(R)H), 126.0 (s, *cis*-C(R)H=C(R)H), 43.7 (s, CH₂), 40.4 (s, CH₂), 32.4 (s, CH₂), 32.3 (s, CH₂), 32.0 (s, CH₂), 29.6 (s, CH₃-*trans* isomer), 24.0, (s, CH₂), 23.9 (s, CH₃-*cis* isomer), 23.1 (s, CH₂), 15.2 (s, CH₃), 15.0 (s, CH₃), 14.6 (s, CH₃), 14.3 (s, CH₃).

4-Methyl-4-nonene. In a 3 L, 3-neck round bottom flask (RBF) equipped with magnetic stirrer and reflux condenser under N₂, ⁿBuLi (100 mL, 1.0 mol, 10.0M in hexanes) was added dropwise *via* a pressure equalising dropping funnel (PEDF) to a THF (1100 mL) solution of Ph₃P(ⁿC₅H₁₁)Br (413 g, 1.0 mol) at 0°C.

After addition was complete, the solution was allowed to warm to RT briefly then re-cooled to 0°C. A solution of 2-pentanone (118 mL, 95 g, 1.1 mol) in THF (200 mL) was added dropwise *via* PEDF. The mixture was allowed to stir and warm to RT overnight. The reaction was quenched carefully *via* dropwise addition of distilled water (500 mL) from a PEDF. The aqueous layer was then extracted with hexanes (3 × 300 mL), and the combined organic fractions dried over MgSO₄, filtered and the volatiles removed *in vacuo*. The crude oil obtained was subjected to a short path distillation to leave a pale yellow liquid. This was then subjected to a fractional distillation to yield the product as a colourless liquid (86.5 g, 62%). Purity = 98.9% (GC). ¹H NMR (CDCl₃, 300.06 MHz) δ_H: 5.30 (m, 1H), 2.18-2.03 (m, 4H), 1.78 (s, 57% of 3H, CH₃), 1.67 (s, 43% of 3H, CH₃), 1.56-1.33 (m, 6H), 1.05-0.91 (m, 6H). ¹³C NMR (CDCl₃, 75.46 MHz) δ_C: 135.3 (s, *trans*-C(R)H=C(R)H), 135.1 (s, *cis*-C(R)H=C(R)H), 126.4 (s, *trans*-C(R)H=C(R)H), 125.6 (s, *cis*-C(R)H=C(R)H), 42.6 (s, CH₂), 34.4 (s, CH₂), 33.1 (s, CH₂), 32.9 (s, CH₂), 28.4 (s, CH₂), 23.9 (s, CH₃), 23.1 (s, CH₂), 21.8 (s, CH₂), 21.7 (s, CH₂), 16.2 (s, CH₃), 14.6 (s, CH₃), 14.5 (s, CH₃), 14.2 (s, CH₃), 14.1 (s, CH₃).

6-Methyl-4-nonene. In a 2 L, 3-neck round bottom flask (RBF) equipped with magnetic stirrer and reflux condenser under N₂, ⁿBuLi (156 mL, 0.25 mol, 1.6M in hexanes) was added dropwise *via* a pressure equalising dropping funnel (PEDF) to a THF (600 mL) solution of Ph₃P(ⁿBu)Br (100 g, 0.25 mol) at 0°C. After addition was complete, the solution was allowed to warm to RT briefly then re-cooled to 0°C. A solution of methylvaleraldehyde (31 mL, 25 g, 0.25 mol) in THF (100 mL) was added dropwise *via* PEDF. The mixture was allowed to stir and warm to RT overnight. The reaction was quenched carefully *via* dropwise addition of distilled water (200 mL) from a PEDF. The aqueous layer was then extracted with hexanes (3 × 300 mL), and the combined organic fractions dried over MgSO₄, filtered and the volatiles removed *in vacuo*. The crude oil obtained was subjected to a short path distillation to leave a pale yellow liquid. This was then subjected to a fractional distillation to yield the product as a colourless liquid (91.7 g, 65%). Purity >99.9% (GC). ¹H NMR (CDCl₃, 300.06 MHz) δ_H: 5.52-5.21 (m, 2H, CH=CH), 2.50 (m, 1H, CH), 2.23-2.01 (m, 2H), 1.54-1.20 (m, 6H), 1.12-0.95 (m, 9H). ¹³C NMR (CDCl₃, 75.46 MHz) δ_C: 137.3 (s, *cis*-C(R)H=C(R)H), 137.1 (s, *trans*-C(R)H=C(R)H), 128.9 (s, *cis*-C(R)H=C(R)H), 128.7 (s, *trans*-C(R)H=C(R)H), 40.6 (s, CH₂), 40.2 (s, CH₂), 37.4 (s, CH-*cis* isomer), 32.1 (s, CH-*trans* isomer), 23.8 (s, CH₂), 23.5 (s, CH₂), 22.0 (s, CH₃-*trans* isomer), 21.6 (s, CH₃-*cis* isomer), 21.4 (s, CH₂), 21.2 (s, CH₂), 14.8 (s, CH₃-*trans* isomer), 14.7 (s, CH₃-*cis* isomer), 14.3 (s, CH₃-*trans* isomer), 14.1 (s, CH₃-*cis* isomer).

6-Methyl-3-nonene. A suspension of Mg turnings (6.18 g, 0.25 mol) and one crystal of I₂ in THF (100 mL) was stirred at RT under N₂. 2-Bromopentane (12.6 mL, 15.38 g, 102 mmol) was added dropwise at a rate that lead to and sustained reflux, after which the mixture was refluxed for 30 minutes, then cooled to 0°C and CuI.PBu₃ (2.00 g, 5.1 mmol) added. 1-Bromo-2-pentene (6.0 mL, 7.59 g, 51 mmol) as a solution in THF (50 mL) was then added dropwise and the vessel stirred at 0°C for 30 minutes, before being allowed to warm to RT overnight. The mixture was carefully quenched with distilled water (200 mL), filtered and extracted with hexanes (5 × 100 mL). The combined organic fractions were dried with MgSO₄, filtered and the solvent removed *in vacuo*. The crude oil obtained was subjected to a short path distillation to leave a pale yellow liquid. This was then subjected to a fractional distillation to yield the product as a colourless liquid (4.22 g, 59%). ¹³C NMR (CDCl₃, 75.46 MHz) δ_C: 141.7 (s, *trans*-C(R)H=C(R)H), 140.4 (s, *cis*-C(R)H=C(R)H), 132.4 (s, *trans*-C(R)H=C(R)H), 128.1 (s, *cis*-C(R)H=C(R)H), 37.5 (s, CH₂), 35.8 (s, CH₂), 36.7 (s, CH), 36.3 (s, CH), 26.7 (s, CH₂), 25.4 (s, CH₂), 20.8 (s, CH₂), 20.5 (s, CH₂), 22.8 (s, CH₃), 17.2 (s, CH₃), 15.5 (s, CH₃), 14.6 (s, CH₃), 14.0 (s, CH₃).

6-Methyl-2-nonene. A suspension of Mg turnings (2.90 g, 0.12 mol) and one crystal of I₂ in THF (50 mL) was stirred at RT under N₂. Crotyl chloride (9.4 mL, 8.64 g, 95 mmol) was added dropwise at a rate that lead to and sustained reflux, after which the mixture was refluxed for 30 minutes, then cooled to 0°C and CuI.PBu₃ (1.87 g, 4.7 mmol) added. 2-Methyl-1-bromopentane (7.88 g, 47 mmol) as a solution in THF (40 mL) was then added dropwise and the vessel stirred at 0°C for 30 minutes, before being allowed to warm to RT overnight. The mixture was carefully quenched with distilled water (200 mL), filtered and extracted with hexanes (5 × 100 mL). The combined organic fractions were dried with MgSO₄, filtered and the solvent removed *in vacuo*. The crude oil obtained was subjected to a short path distillation to leave a pale yellow liquid. This was then subjected to a fractional distillation to yield the product as a colourless liquid (2.84 g, 43%). ¹³C NMR (CDCl₃, 75.46 MHz) δ_C: 132.1 (s, *trans*-C(R)H=C(Me)H), 131.3 (s, *cis*-C(R)H=C(Me)H), 124.5 (s, *trans*-C(R)H=C(Me)H), 123.6 (s, *cis*-C(R)H=C(Me)H), 39.5 (s, CH₂), 37.2 (s, CH₂), 37.1 (s, CH₂), 32.4 (s, CH), 32.2 (s, CH), 30.4 (s, CH₂), 24.6 (s, CH₂), 22.8 (s, CH₃), 20.2 (s, CH₂), 20.1 (s, CH₂), 19.7 (s, CH₃), 18.1 (s, CH₃), 14.6 (s, CH₃), 14.0 (s, CH₃), 12.8 (s, CH₃).

6-Methyl-1-nonene. A suspension of Mg turnings (7.09 g, 0.29 mol) and one crystal of I₂ in THF (150 mL) was stirred at RT under N₂. 2-methyl-1-bromopentane (19.3 g, 0.12 mol) was added dropwise at a rate that lead to, and sustained, reflux, after which the mixture was refluxed for 30 minutes, then cooled to 0°C and CuI.PBu₃ (2.3 g, 6 mmol) added. 4-bromo-1-butene (6.2 mL, 8.2 g, 0.06 mol) as a solution in THF (50 mL) was then added dropwise and the vessel stirred at 0°C for 30 minutes, before being allowed to warm to RT

overnight. The mixture was carefully quenched with distilled water (250 mL), filtered and extracted with hexanes (5 × 100 mL). The combined organic fractions were dried with MgSO₄, filtered and the solvent removed *in vacuo*. The crude oil obtained was subjected to a short path distillation to leave a pale yellow liquid. This was then subjected to a fractional distillation to yield the product as a colourless liquid (3.98 g, 47%). ¹³C NMR (CDCl₃, 75.46 MHz) δ_C: 139.4 (s, C(R)H=CH₂), 114.3 (s, C(R)H=CH₂), 39.6 (s, CH₂), 36.8 (s, CH₂), 34.4 (s, CH₂), 32.6 (s, CH), 26.6 (s, CH₂), 20.3 (s, CH₂), 19.8 (s, CH₃), 14.6 (s, CH₃).

2-Propyl-1-heptene. In a 3 L, 3-neck round bottom flask (RBF) equipped with magnetic stirrer and reflux condenser under N₂, ⁿBuLi (100 mL, 1.0 mol, 10.0M in hexanes) was added dropwise *via* a pressure equalising dropping funnel (PEDF) to a THF (1000 mL) solution of Ph₃P(Me)Br (357 g, 1.0 mol) at 0°C. After addition was complete, the solution was allowed to warm to RT briefly, then re-cooled to 0°C. A solution of 4-nonanone (173 mL, 142 g, 1.0 mol) in THF (200 mL) was added dropwise *via* PEDF. The mixture was allowed to stir and warm to RT overnight. The reaction was quenched carefully *via* dropwise addition of distilled water (500 mL) from a PEDF. The aqueous layer was then extracted with hexanes (3 × 300 mL), and the combined organic fractions dried over MgSO₄, filtered and the volatiles removed *in vacuo*. The crude oil obtained was subjected to a short path distillation to leave a pale yellow liquid. This was then subjected to a fractional distillation to yield the product as a colourless liquid (80.9 g, 58%). Purity = 98.9% (GC). ¹H NMR (CDCl₃, 300.06 MHz) δ_H: 4.86 (br s, 2H), 2.10-2.00 (m, 4H), 1.59-1.27 (m, 8H), 1.03-0.94 (m, 6H). ¹³C NMR (CDCl₃, 75.46 MHz) δ_C: 150.1 (s, C=CH₂), 109.6 (s, C=CH₂), 38.9 (s, CH₂), 36.7 (s, CH₂), 32.4 (s, CH₂), 28.3 (s, CH₂), 23.4 (s, CH₂), 21.6 (s, CH₂), 14.7 (s, CH₃), 14.4 (s, CH₃).

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