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Iridium-catalysed isomerising trialkylsilylation of methyl oleate☆

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ABSTRACT

Monounsaturated fatty acids from vegetable oils are attractive substrates for applications as renewable feedstock in polymer industry. Applying the concept of transition metal-catalysed isomerising functionalisation, their nearly inaccessible internal C=C double bond can be transformed into products with a functional group in the terminal position. In this work, methyl oleate is shown to undergo [Ir(OMe)(cod)]$_2$-catalysed dehydrogenative silylation with triethylsilane to give terminal vinylsilanes **4** in 69% yield. Independent preparation of reference substances is helpful in identifying the desired products in gas chromatograms of complex reaction mixtures.

1. Introduction

Unsaturated fatty acid methyl esters derived from natural oils are an attractive feedstock for the fabrication of higher-value chemicals because of their increasing availability due to the large-scale production of biodiesel fuel [1]. The majority of these naturally occurring unsaturated fatty esters are characterised by an internal double bond at the site of carbon number nine or higher [2], methyl oleate being the most prominent example.

Obviously, the position of the double bond deep inside the molecule is unfavourable with respect to use of this renewable feedstock in the polymer industry [3]. A double bond situated at the ω-terminal end of the carbon chain would be desirable, for reasons of both accessibility and atom economy. For example, methyl ricinoleate from castor oil is pyrolysed in high tonnage to yield methyl undecenoate, a terminally unsaturated fatty ester, which is transformed into ω-aminoundecanoic acid and subsequently polymerised to the polyamide nylon 11 (Rilsan®) [4]. This is not a generalisable case, however, on account of the special chemistry of ricinoleic acid. The amount of other natural fatty acids with terminal double bonds, such as orophetic acid from the leaves of *Orophea enneandra* or isanic acid from *Olacaceae*, is negligible, as the relevant plant sources are scarce [5].

However, this problem can be circumvented by adapting the concept of transition metal-catalysed isomerising functionalisation. In this tandem reaction type, the substrate is converted into an equilibrium mixture of positional and geometrical isomers by a number of double bond migration and isomerisation steps. From this rapidly interconverting pool of all possible isomers (31 in the case of methyl oleate) only one is specifically trapped out of the equilibrium by selective functionalisation. In many cases, the transition metal complex plays a double role in catalysing both of the abovementioned steps. According to Le Chatelier's principle, this combination of equilibrium isomerisation and irreversible functionalisation can achieve high yields of the desired product even though the respective positional isomer is present in only minimal amounts [6]. For oleic acid and its esters, such processes have been known since 2005, when Behr et al. reported on a rhodium-catalysed ω-selective hydroformylation [7]. In addition, palladium-catalysed ω-alcoxycarbonylation was presented by Jiménez-Rodriguez et al. [8]. Iridium-catalysed ω-hydroboration was reported by Ghebreyessus and Angelici [9]. More recently, Gooßen et al. commented on silver-catalysed selective functionalisation of the 4-position to yield γ-lactones [10] as well as rhodium-catalysed conjugate addition of aryl and amine groups to afford β-arylated and β-amino acids (Scheme 1) [11]. In the interim, papers have been published on polymerisation of the obtained monomers [12], expansion of the range of substrates to commercial triglycerides [13], mechanistic features [6e], and on improvement of some of these processes using ionic liquids [14] and water as solvent [15].

Nevertheless, to the best of our knowledge, there have been no reports of an analogous process for the selective addition of silicon-containing groups to fatty acids or esters, although there are indications of a similar reaction with simpler olefins [16]. Along with their expected high biocompatibility and low environmental

☆ This paper is dedicated to Professor Wolfgang A. Herrmann on the occasion of his 65th birthday.

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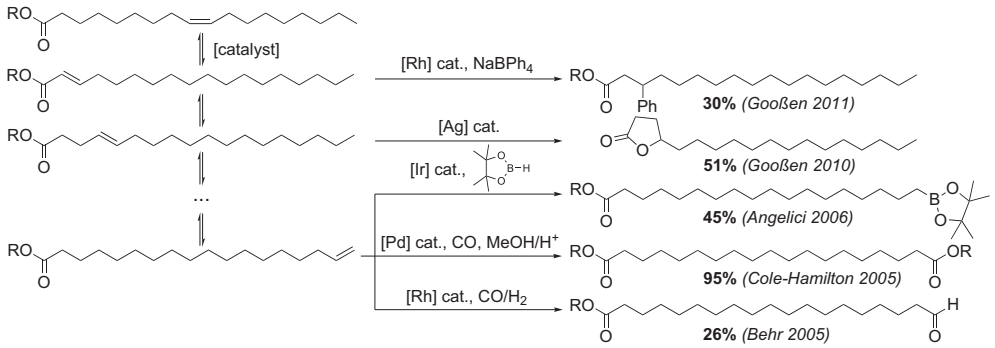


Scheme 1. Outline of important isomerising functionalisations of fatty acids and esters reported in the literature.

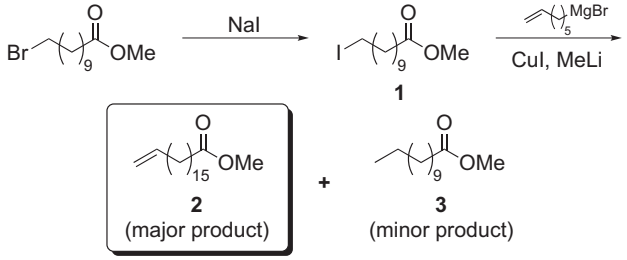
impact [17], such silicon oleochemicals would be of interest for their wide range of applications as adhesives, coupling agents, lubricants, plasticisers, and monomers for the production of silicon-containing polymers [18]. Organosilicon compounds are predominantly prepared by direct synthesis [19] and hydrosilylation [20]. First results of hydrosilane addition to internally unsaturated fatty acid esters were published as early as 1955 by Speier, followed by a few others, but no ω-substituted products whatsoever were obtained [21]. In the last two decades, other reactions of silanes catalysed by transition metal complexes have been revealed, notably dehydrogenative silylation of terminal alkenes to produce vinylsilanes [22]. Herein, we offer an Ir(I)-catalysed dehydrogenative silylation of methyl oleate with triethylsilane leading to good yields of terminal products.

2. Results and discussion

2.1. Synthesis of reference compounds

Preliminary results of isomerising silylation reactions most often showed complicated mixtures of products that were inseparable by conventional techniques and thus scarcely isolable for NMR analysis. Therefore, our first step was to synthesise the respective target compounds to have reference substances at hand that allow for unequivocal identification in gas chromatographic (GC) analyses of complex reaction mixtures. Consequently, a sample of methyl octadec-17-enoate (**2**), the positional isomer of methyl oleate bearing a terminal double bond, was essential.

It is a well-known compound that has been synthesised in many different ways [23], including the "acetylene zipper" method [24] and the reaction of iodo esters with mixed dialkylcuprates [25]. We tried to reproduce this by preparing methyl 11-iodoundecanoate (**1**) from methyl 11-bromoundecanoate and sodium iodide in refluxing acetone and subsequently reacting it with a preformed mixed dialkylcuprate from hept-6-en-1-ylmagnesium bromide and methylcopper (Scheme 2). Our problem was that a substantial amount (9% calculated by GC peak area) of by-product



Scheme 2. Synthetic route to methyl octadec-17-enoate (**2**).

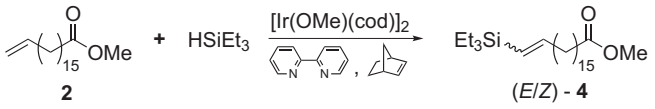
eluting from GC column at 8.8 min remained even after intensive column chromatographic purification of **2**. This contamination turned out to be methyl dodecanoate (**3**), formed by methyl group transfer from the mixed dialkylcuprate to the iodo ester **1**, an unwanted side-reaction that is known from the literature [25b]. On normal phase silica gel, **2** and **3** showed identical R_f values and thus could not be separated by column and thin layer chromatography (TLC). Roomi et al.'s suggestion of using reversed phase TLC for the separation of saturated from unsaturated fatty acid esters [26] proved viable for solving this problem as well. For **2** and **3**, R_f values were found to be 0.22 and 0.43, respectively, using RP-18 modified plates and pure acetonitrile as eluent. This difference appeared promising enough for us to extend the scope of this separation problem to preparative scale: the use of solid phase extraction (SPE) cartridges with octadecyl-modified silica phases served for this purpose. We were pleased to find that separations were excellent even in large scale with a 10 g cartridge and more than 230 mg of crude product, recovering up to 96% of pure ester **2** without any quantifiable contamination present. A discontinuous gradient from acetonitrile–water (9:1) to pure acetonitrile proved to be the eluent of choice.

With pure **2** available, we were able to prepare methyl 18-(triethylsilyl)octadec-17-enoate (**4**) by bis(1,5-cyclooctadiene)di-μ-methoxydiiridium(I)-catalysed dehydrogenative silylation following a procedure published by Lu and Falck [27] (Scheme 3). Vinylsilane **4** was of special interest to us as it would be the desired product formed in a potential ω-selective isomerising dehydrogenative silylation starting from internally unsaturated methyl oleate.

Good *Z*-diastereoselectivity of this reaction is described with 2,2′-bipyridine-based ligands bearing sterically demanding *tert*-butyl groups. In contrast to this, we used simple 2,2′-bipyridine and slightly prolonged reaction time, as we had to prepare both geometrical isomers in substantial quantities. In this way, **4** was obtained as an *E*/*Z* isomeric mixture in a ratio of about 1:4 (calculated by GC peak area). The two isomers were well separated by GC, with retention times of 27.4 min and 27.6 min for (*E*)-**4** and (*Z*)-**4**, respectively. Their identical mass spectra showed no distinct peaks in the range from $m/z = 202$ to 348, indicating that silylation took place on the terminal carbon. This could be confirmed by ^{1}H NMR analysis, in which **4** showed four signals with characteristic multiplets in the olefinic region, accounting for both alkene protons of the *E* and *Z* isomer, respectively.

In order to be able to distinguish vinylsilanes **4** from the corresponding internally substituted isomers **5b**, we also tried to prepare these by [Cp*Ru(MeCN)$_3$]PF$_6$-catalysed hydrosilylation of octadec-9-ynoic acid with triethylsilane (Scheme 4).

Hydrosilylation of long-chain internal alkynes seemed to be somewhat difficult due to the lack of suitable catalysts, but Trost and Ball's procedure [28] turned out to meet our demands.



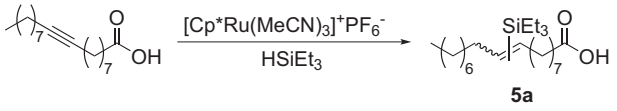
Scheme 3. Synthesis of methyl 18-(triethylsilyl)octadec-17-enoate (**4**).

Theoretically speaking, hydrosilylation of such substrates can provide up to four isomers with the silyl group attached to either carbon of the C=C double bond in *E* or *Z* geometry. In terms of stereoselectivity, Ball and Trost reported extremely robust *Z*-selectivity for the said ruthenium catalyst, whereas regioselectivity was expected to be poor owing to the long alkyl chains at either side of the double bond. In line with these expectations, ^{1}H NMR of acids **5a** showed a single triplet for the alkene proton, while ^{13}C NMR showed double peaks for each olefinic carbon. This suggests that we obtained **5a** as a mixture of two (*Z*)-configured regioisomers with the triethylsilyl group attached to carbon number nine or ten. For GC analysis, we esterified acids **5a** in methanol to obtain methyl esters **5b**. Surprisingly, the GC of **5b** showed a single peak eluting at 26.6 min, indicating that both regioisomers have identical retention times in the system used. The mass spectrum of **5b** revealed a distinct peak at $m/z = 253$, which clearly precludes substitution at carbons other than nine and ten.

2.2. Tandem isomerisation-silylation

When we tried to extend the method for dehydrogenative trialkylsilylation [27] of terminal double bonds to long-chain internal olefins, such as methyl oleate, it was to be expected that this reaction would be too sluggish to be useful. Initially, we used exactly the same composition as Lu and Falck, consisting of one equivalent of methyl oleate, 5 mol% of iridium catalyst, 10 mol% of 2,2′-bipyridine-based ligand and three equivalents each of norbornene and triethylsilane. After stirring at 60 °C for 48 h, GC of the reaction mixture showed a number of peaks in the region from 7.0 to 14.5 min, resulting from single and double silylation and eventual hydrogenation of norbornene. These peaks are excluded from the following quantification due to the large excess of sacrificial alkene and silane used. In addition, the GC showed mainly peaks of unreacted substrate and only a minor peak in the product region, eluting from column at 26.5 min. This was quantified to constitute 15% (calculated by GC peak area, based on one equivalent of methyl oleate) and identified as internal product **5b** by comparison of retention time and mass spectrum with the respective reference compound. Indeed, this outcome is in accordance with Lu and Falck's assertion that 2,2′-bipyridine-based ligands may inhibit any isomerisation of olefin and thereby retain the double bond at the initial position, making only unreactive internal olefin available for silylation and giving rise to only 15% of product even after a prolonged period of heating.

In the course of our investigations the question arose how simple omission of the bipyridine ligand would affect the reaction system. We were pleased to find that this measure dramatically boosted the reaction. Best results were then obtained with 24 h of stirring at 60 °C and a catalyst loading of 8 mol%. After that time, a total of 12% of unreacted substrate methyl oleate and its positional isomers, 6% of hydrogenation product methyl stearate, 8% of internally silylated products **5b** and 6% of unidentified products



Scheme 4. Preparation of internally silylated acids **5a**.

were present in the reaction mixture. The majority of 69% consisted of two peaks eluting at 27.4 and 27.6 min. By comparison of GC–MS data with our independently synthesised reference compounds, these two were assigned to terminal vinylsilanes (*E*/*Z*)-**4**. Again, quantifications are based on GC peak areas referred to one equivalent of methyl oleate, while peaks resulting from reactions on excess sacrificial alkene were excluded. The aforementioned composition of the reaction system is a result of our efforts to optimise the reaction conditions. Lowering the catalyst loading to values of 5 mol% and below led to a significant decrease in product yield, giving rise to less than 50% of **4**. An even more negative effect on product yield was observed when we tried to decrease the amount of norbornene in the mixture. Generally, a temperature of 60 °C was necessary to form reasonable quantities of products within 24 h. However, markedly increasing the temperature caused a complete breakdown of the catalyst system. Instead of triethylsilane, we also tried to use hydrosilanes bearing more sterically hindered alkyl substituents in order to enhance the silylation selectivity for the terminal products. Unfortunately, only trace amounts of products could be detected using triisopropylsilane and *tert*-butyldimethylsilane.

The above results show that the internal double bond of methyl oleate isomerises in the presence of catalyst $[Ir(OMe)(cod)]_2$ and that the terminal positional isomer selectively undergoes dehydrogenative trialkylsilylation to give the terminal vinylsilanes **4** in good yield. Obviously, the iridium catalyst plays a double role in this tandem process by promoting both isomerisation and silylation. The use of norbornene as sacrificial alkene, which acts as hydrogen acceptor, was crucial for this reaction. Unfortunately, more sterically hindered silanes, for example triisopropylsilane, turned out to be unreactive using this protocol. When additional catalysts or ligands were used that might facilitate isomerisation, any silylation activity of the system collapsed.

3. Conclusion

The goal of this project was to establish an isomerising silylation reaction starting from methyl oleate that would give a product in which the trialkylsilyl group is on the terminal carbon. A system comprising $[Ir(OMe)(cod)]_2$ catalyst and norbornene gave rise to the desired product in 69% yield. The identification of substances was facilitated by independent preparation of reference compounds. Our results suggest that also other monounsaturated fatty acid esters, especially mixtures of positional isomers obtained by partial hydrogenation of vegetable oils, can be similarly transformed into the same terminal vinylsilanes **4**. Studies are on the way to improve the process by catalyst tuning and extend the scope of the reaction by applying hydrosilanes with different polarity.

4. Experimental section

4.1. General remarks

All reactions and manipulations were carried out under an argon atmosphere (Westfalen, 5.0) using standard Schlenk techniques and flame-dried glassware, except where otherwise noted. All solvents used during this work were of p.a. grade, anhydrous solvents were purchased from VWR, deuterated solvents from Deutero. $[Ir(OMe)(cod)]_2$ was from Umicore, $[Cp^*Ru(MeCN)_3]PF_6$ was from Strem. Methyl 11-bromoundecanoate (95%), magnesium granules (98%), 7-bromo-1-heptene (97%), methyllithium solution, methyl oleate (99%), triethylsilane (99%) and norbornene (99%) were from Sigma Aldrich. 2,2′-Bipyridine (99%) and octadec-9-ynoic acid (98%) were from Alfa Aesar. Copper(I) iodide (99.999%) and anhydrous sodium iodide (99%) were from ABCR. Boron

trifluoride diethyl ether complex (for synthesis) was from Merck. All commercial reagents were used as received without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECS 400 spectrometer. Chemical shifts are given as dimensionless δ values and are frequency-referenced to the peak of tetramethylsilane ($\delta = 0$ ppm). Coupling constants J are reported in hertz. The multiplicity of the signals is indicated as "s", "brs", "t", "q", "qui" or "m" for singlet, broad singlet, triplet, quartet, quintet or multiplet, respectively. GC–MS data were obtained on an Agilent Technologies HP 6890 GC system with HP 5973 mass selective detector using an HP-5 ms capillary column (30 m × 0.25 mm × 0.25 μm), a helium carrier gas flow rate of 1 mL min^{-1} and a time program starting from 50 °C, hold for 1 min, heating to 100 °C at a rate of 15 °C min^{-1}, heating to 200 °C at a rate of 25 °C min^{-1}, hold for 14 min, heating to 300 °C at a rate of 25 °C min^{-1}, hold for 5 min. Normal and reversed phase TLC were performed on Merck aluminium sheets coated with silica gel 60 and silica gel 60 RP-18 F_{254s}, respectively. Compounds were visualised by dipping in 1 M sulphuric acid solution and subsequent heating. Flash column chromatographic purifications were conducted on silica gel 60 (40–63 μm) obtained from VWR. Solid phase extraction was performed using Chromabond® C_{18} ec cartridges from Macherey–Nagel.

4.2. Synthesis of reference compounds

Following literature-known procedures [25b,c], methyl octadec-17-enoate (**2**) was prepared in two steps.

4.2.1. Methyl 11-iodoundecanoate **1**

A suspension of methyl 11-bromoundecanoate (2.88 g, 10.30 mmol) and sodium iodide (4.77 g, 31.82 mmol) in acetone (100 mL) was heated under reflux for 4 h. After cooling to room temperature, the white salt was filtered off. The filtrate was concentrated under reduced pressure, then water (50 mL) was added. The mixture was extracted with dichloromethane. The combined organic extracts were washed successively with 10 wt% aqueous sodium thiosulphate and brine, dried over anhydrous magnesium sulphate, filtered and concentrated under reduced pressure to yield **1** as a light yellow oil (3.18 g, 95%) that was used without further purification. TLC (*n*-hexane–diethyl ether 9:1): R_f 0.35. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.64 (3H, s), 3.16 (2H, t, $J = 7.0$ Hz), 2.28 (2H, t, $J = 7.5$ Hz), 1.83–1.76 (2H, m), 1.59 (2H, qui, $J = 7.4$ Hz), 1.38–1.23 (12H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.4, 51.5, 34.2, 33.6, 30.5, 29.4, 29.3, 29.2, 28.6, 25.0, 7.4. GC: t_R 12.2 min. EIMS (70 eV): *m*/*z* (%) 326 (1), 295 (39), 199 (100), 167 (83), 149 (82), 83 (76), 69 (74), 55 (77).

4.2.2. Methyl octadec-17-enoate **2**

Grignard reagent hept-6-en-1-ylmagnesium bromide was prepared by suspending magnesium granules (0.22 g, 9.05 mmol) in anhydrous tetrahydrofuran (20 mL) and subsequently adding 7-bromo-1-heptene (1.63 g, 9.19 mmol) dropwise. The mixture was refluxed for 30 min. In a separate flask, copper(I) iodide (1.72 g, 9.03 mmol) was suspended in anhydrous tetrahydrofuran (10 mL) and cooled to −78 °C in an isopropyl alcohol–dry ice bath. Methyllithium solution (1.6 M in diethyl ether, 5.65 mL, 9.04 mmol) was added very slowly via syringe. The resultant mixture was stirred at −78 °C for 1 h and then slowly allowed to warm to 0 °C, whereupon a brownish suspension formed, which was immediately cooled to −78 °C. After that, the aforementioned solution of Grignard reagent in tetrahydrofuran was added via syringe. The mixture thus obtained was stirred at −78 °C for 1 h and then allowed to warm to 0 °C, whereupon a purple colouration appeared. The mixture was then cooled again to −78 °C and a solution of **1** (1.47 g, 4.51 mmol) in tetrahydrofuran (20 mL) was added via syringe. That mixture was allowed to stir at −78 °C for 1 h and at room temperature for 2 h, and the reaction was quenched by adding saturated aqueous ammonium chloride (15 mL). After addition of diethyl ether (50 mL), two layers and a brown insoluble formed which was filtered off. The organic phase was separated and the royal blue aqueous phase was extracted with diethyl ether. The combined organic fractions were washed with brine, dried over anhydrous magnesium sulphate, filtered and concentrated under reduced pressure. Flash column chromatography of the residual brown oil with *n*-hexane–diethyl ether (95:5) yielded the crude ester mixture (0.56 g, 42%). A 0.23 g portion was separated from the by-product **3** by passing over a 10 g SPE cartridge. Step gradient elution from acetonitrile–water (9:1) to pure acetonitrile yielded pure ester **2** as a white solid (0.20 g, 96%) after concentration under reduced pressure. TLC (*n*-hexane–diethyl ether 9:1): R_f 0.43. RP-TLC (acetonitrile): R_f 0.22. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.80 (1H, ddt, $J = 16.9, 10.1, 6.6$ Hz), 5.00–4.89 (2H, m), 3.65 (3H, s), 2.28 (2H, t, $J = 7.4$ Hz), 2.05–1.99 (2H, m), 1.60 (2H, qui, $J = 7.3$ Hz), 1.38–1.20 (24H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.4, 139.3, 114.1, 51.5, 34.2, 33.9, 29.7 (3), 29.6, 29.5, 29.3, 29.2, 29.0, 25.0. GC: t_R 16.6 min. EIMS (70 eV): *m*/*z* (%) 296 (1), 264 (51), 222 (28), 180 (19), 111 (19), 97 (45), 87 (59), 74 (83), 55 (100), 41 (58).

4.2.3. Methyl 18-(triethylsilyl)octadec-17-enoate **4**

Adapting Lu and Falck's procedure, terminal olefin **2** (41 mg, 0.14 mmol), $[Ir(OMe)(cod)]_2$ (5 mg, 0.01 mmol), 2,2′-bipyridine (3 mg, 0.02 mmol) and norbornene (40 mg, 0.43 mmol) were dissolved in anhydrous tetrahydrofuran (1 mL). After stirring for 5 min, triethylsilane (0.14 mL, 0.91 mmol) was added dropwise via syringe, and the reaction mixture was stirred at 40 °C for 2 h. Concentration under reduced pressure and flash column chromatography of the residual oil with *n*-hexane–diethyl ether (9:1) gave the vinylsilanes **4** as an *E*/*Z*-diastereomeric mixture (41 mg, 72%). TLC (*n*-hexane–diethyl ether 9:1): R_f 0.37. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.35 (0.9H, dt, $J = 14.3, 7.3$ Hz), 6.00 (0.1H, dt, $J = 18.7, 6.3$ Hz), 5.51 (0.1H, d, $J = 18.7$ Hz), 5.36 (0.9H, d, $J = 14.1$ Hz), 3.65 (3H, s), 2.28 (2H, t, $J = 7.6$ Hz), 2.14–2.04 (2H, m), 1.65–1.56 (2H, m), 1.36–1.20 (24H, m), 0.98–0.84 (9H, m), 0.61–0.51 (6H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.4, 150.5, 148.9, 125.5, 124.9, 51.5, 37.1, 34.2, 32.0, 29.9, 29.7 (2), 29.5 (2), 29.3, 29.2, 25.0, 7.6, 7.5, 4.8, 3.6. GC: t_R 27.4, 27.6 min. EIMS (70 eV): *m*/*z* (%) 410 (1), 381 (100), 349 (7), 201 (5), 117 (59), 115 (15), 87 (27), 59 (16).

4.2.4. Mixture of isomeric 9-(triethylsilyl)octadec-9-enoic and 10-(triethylsilyl)octadec-9-enoic acids **5a**

Adapting Trost and Ball's procedure [28], octadec-9-ynoic acid (90 mg, 0.32 mmol) was dissolved in anhydrous dichloromethane (1 mL). The mixture was cooled to 0 °C and triethylsilane (0.06 mL, 0.38 mmol) was added via syringe. Immediately after $[Cp^*Ru(MeCN)_3]PF_6$ (5 mg, 0.01 mmol) was added, the ice bath was removed and the flask was stirred at room temperature for 2 h. The crude reaction mixture was concentrated under reduced pressure and purified by flash column chromatography with *n*-hexane–diethyl ether–acetic acid (80:20:1) as eluent to yield pure acids **5a** as a light yellow oil (103 mg, 81%). TLC (*n*-hexane–diethyl ether–acetic acid 80:20:1): R_f 0.2. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.49 (1H, brs), 5.96 (1H, t, $J = 7.2$ Hz), 2.33 (2H, t, $J = 7.4$ Hz), 2.08–2.03 (2H, m), 1.96 (2H, brs), 1.68–1.56 (2H, m), 1.38–1.21 (20H, m), 0.94–0.85 (12H, m), 0.63 (6H, q, $J = 7.9$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.6 (2), 144.2, 143.9, 136.4, 136.1, 38.5, 38.4, 34.2, 32.2, 32.1, 32.0, 31.2, 31.1, 30.3, 30.2, 29.7, 29.6, 29.4 (2), 29.3, 29.2 (2), 29.1, 24.7, 22.8, 14.2, 7.7, 4.3. Esterification was necessary for GC–MS characterisation: an aliquot of acids **5a** was dissolved in methanol, mixed with few drops of boron trifluoride diethyl etherate, heated to 70 °C

for 30 min, cooled to room temperature and injected directly. GC of the methyl esters **5b**: t_R 26.6 min. EIMS (70 eV): *m/z* (%) 410 (9), 381 (100), 349 (31), 294 (5), 281 (6), 253 (5), 207 (26), 201 (15), 173 (5), 135 (12), 117 (78), 115 (32), 103 (37), 87 (66), 59 (47), 43 (14).

4.3. Tandem isomerisation-triethylsilylation

$[Ir(OMe)(cod)]_2$ (8 mg, 0.01 mmol), methyl oleate (43 mg, 0.15 mmol) and norbornene (41 mg, 0.44 mmol) were dissolved in anhydrous tetrahydrofuran (1 mL). After stirring for 5 min, triethylsilane (0.07 mL, 0.44 mmol) was added dropwise via syringe, and the reaction mixture was stirred at 60 °C for 24 h. The resulting solution was diluted with acetone (10 mL), filtered through silica gel to remove the catalyst and subjected directly to GC–MS analysis.

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