Electronic Supplementary Material (ESI) for RSC Sustainability.

Supporting Information for:

Direct Chemoselective Reduction of Plant Oils using Silane Catalysed by Rh(III) Complex at Ambient Temperature

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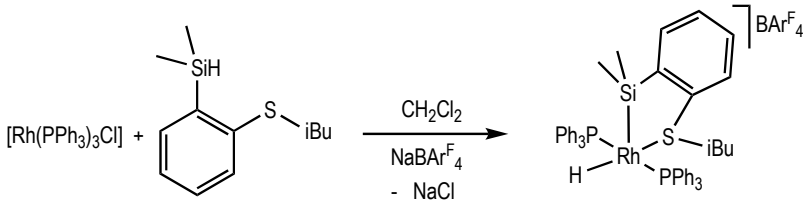
1. General Procedures

All manipulations, unless otherwise stated, were performed under an atmosphere of nitrogen, using standard Schlenk techniques. Glassware was oven dried at 110ºC overnight and flamed under vacuum prior to use. Dry and oxygen free solvents were employed.

[Rh(SiS^{i}Bu)]: The precatalyst used, {Rh(H)[SiMe$_2$(o-C$_6$H$_4$S^{i}Bu)](PPh$_3$)$_2$}[BAr$^F_4$] (**[Rh(SiS^{i}Bu)]**) was prepared as previously reported.[1]



Scheme S.1. Synthesis of the precatalysts **[Rh(SiS^{i}Bu)]**

Substrates: The substrates used in the catalytic reactions were purchased from the commercial companies below and used without any pre-treatment:

- Triethylsilane: Merck
- Diphenylsilane: Merck
- 1-octene: Merck
- Cis-2-octene: Merck
- 5-hexenylacetate: Merck
- Ethyl oleate: Merck
- Olive oil: Tesco Supermarket
- Coconut oil: Tesco Supermarket
- Castor oil: Tesco Supermarket
- Sesame oil: Tesco Supermarket
- Sunflower oil: Tesco Supermarket

NMR: NMR spectra were recorded on Bruker Advance DPX 300 MHz spectrometer. ^{1}H NMR spectra were referenced to the residual solvent signals. Chemical shifts are quoted in ppm and coupling constants in Hz.

GC-MS: Samples for GC-MS measurements were prepared in HPLC grade DCM and the measurements were conducted on an Agilent 8860 GC system coupled to an Agilent 5977B EI instrument.

Catalytic Experiments: All catalytic experiments were carried under an inert atmosphere, at room temperature, using 0.5 mol% catalyst in neat. After the reaction time, the corresponding amount of internal standard was added and the composition of the reaction mixture was analyzed by ^{1}H NMR in $CDCl_3$.

Internal standard: 1,2-dichloroethane (0.25 equivalents) in the case of reactions performed using octenes, ethyl acetate, methyl 5-hexenoate and ethyl oleate.
1,1,2,2-tetrachloroethane (0.5 equivalents by fatty ester chain) in the case of reaction performed using plant oils.

Calculation of yield: Yields were calculated by integrating one of the signals of the product formed except the case of the reaction of octenes, which were calculated by integrating the remaining triethylsilane Si–H signals.

2. Hydrosilylation of 1-octene and cis-2-octene with different silanes using [Rh(SiS^{i}Bu)] as catalyst.

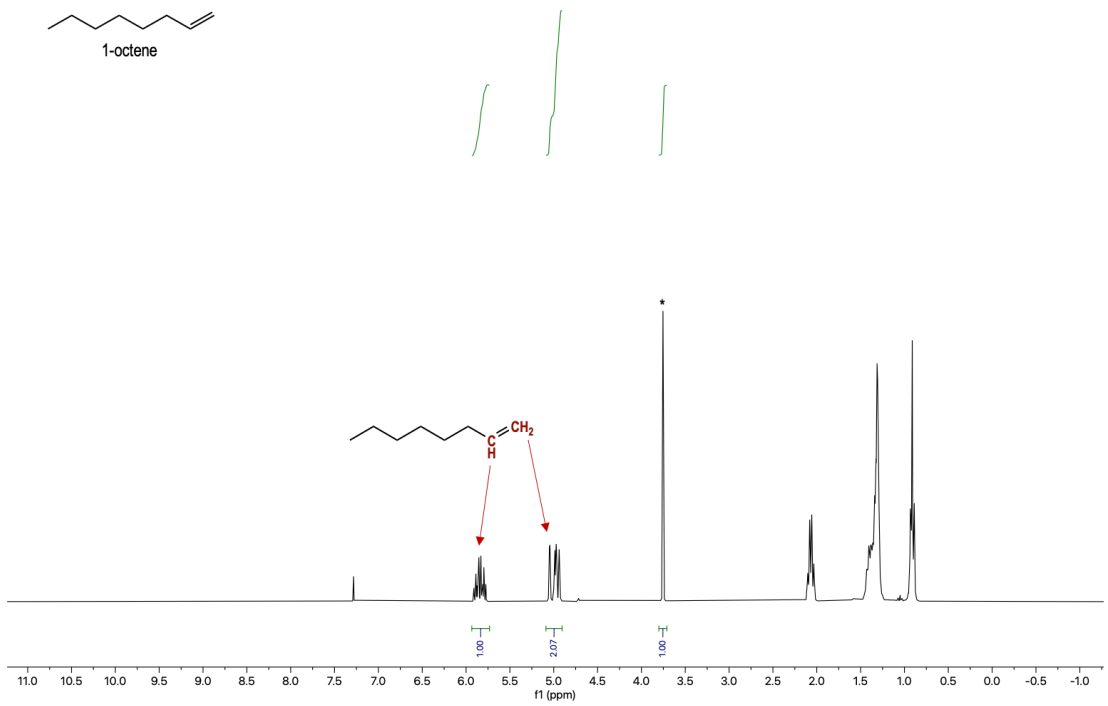


Figure S.1. ^{1}H NMR ($CDCl_3$, 298 K) spectrum of 1-octene. (*) 1,2-dichloroethane (0.25 equivalents) as internal standard.

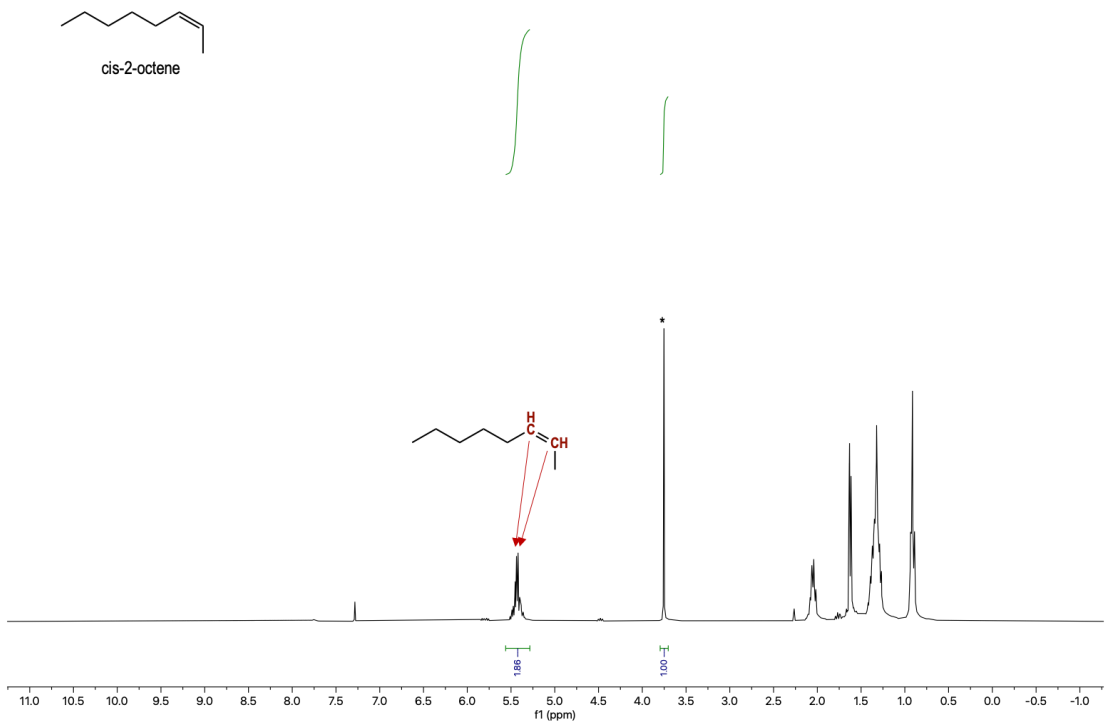


Figure S.2. ^{1}H NMR ($CDCl_3$, 298 K) spectrum of cis-2-octene. (*) 1,2-dichloroethane (0.25 equivalents) as internal standard.

Hydrosilylation of 1-octene using Et_3SiH (Table 1, entry 1)

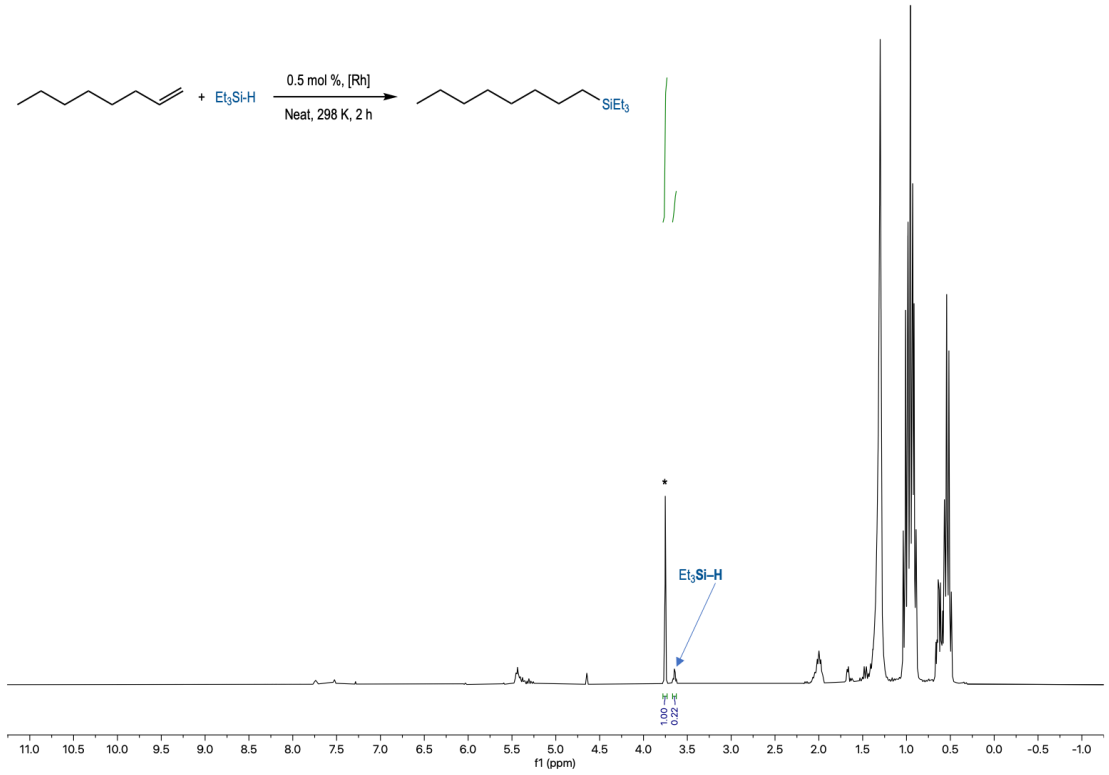


Figure S.3. ^1H NMR ($CDCl_3$, 298 K) spectrum of the crude reaction mixture after 2 hours. (*) 1,2-dichloroethane (0.25 equivalents) as internal standard.

Hydrosilylation of cis-2-octene using Et_3SiH (Table 1, entry 2). From reference 1.

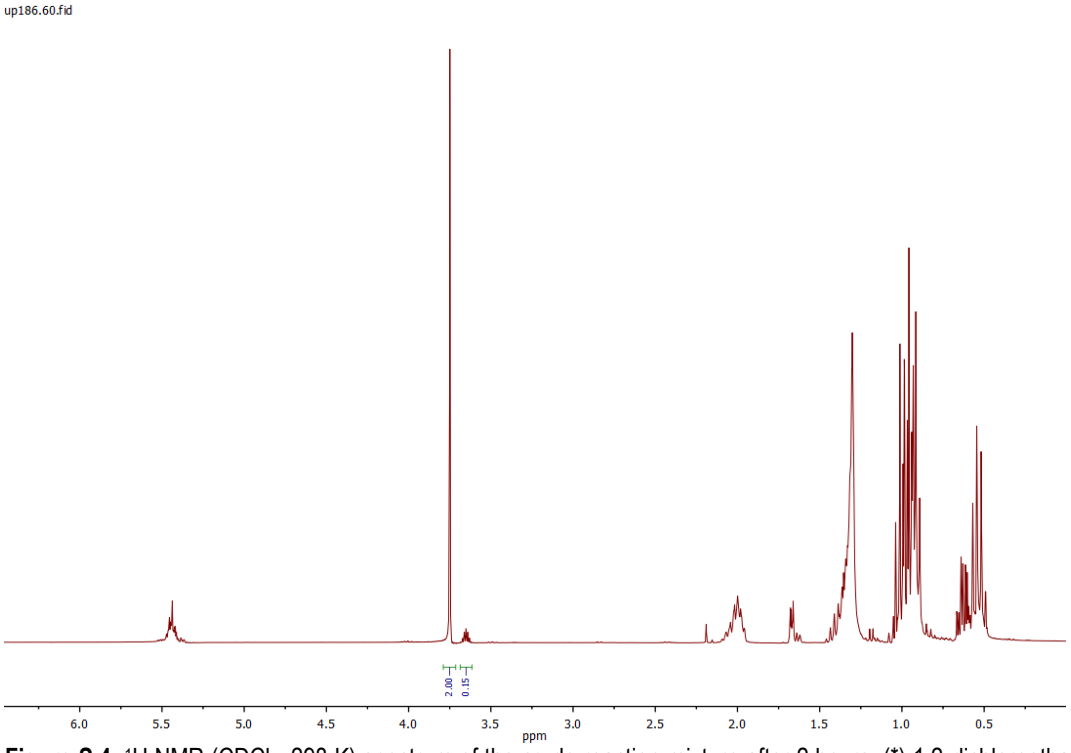


Figure S.4. ^1H NMR ($CDCl_3$, 298 K) spectrum of the crude reaction mixture after 2 hours. (*) 1,2-dichloroethane (0.5 equivalents) as internal standard.

Hydrosilylation of 1-octene using Ph_3SiH (Table 1, entry 3)

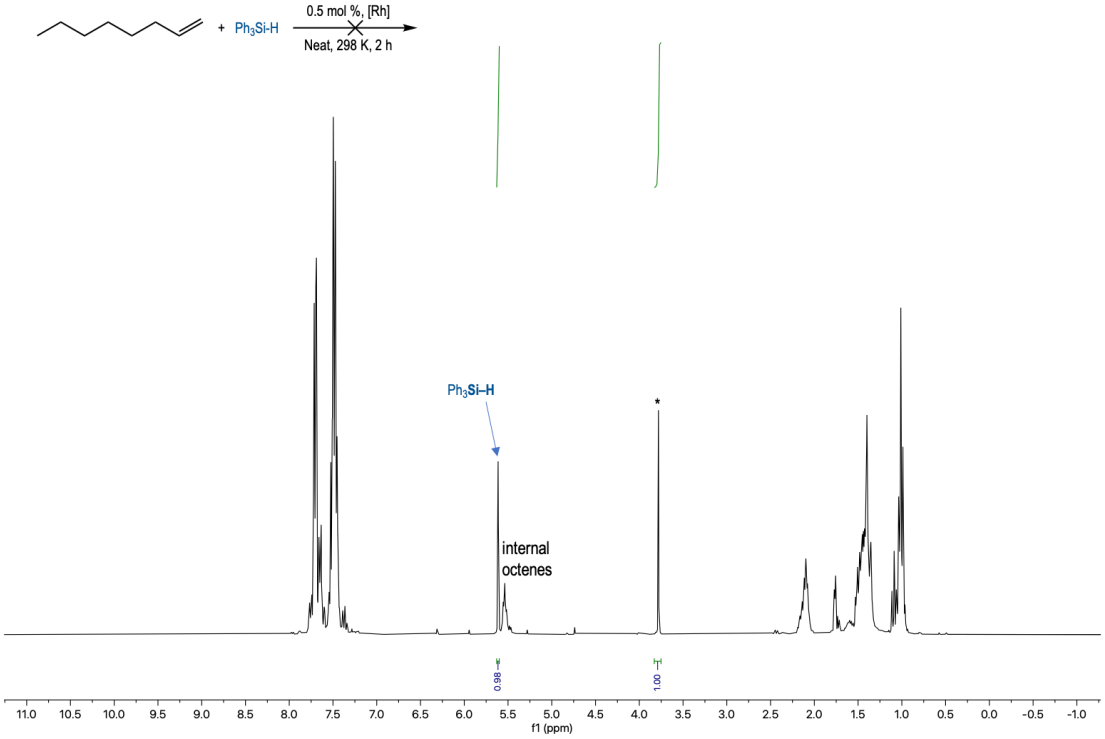


Figure S.5. ^1H NMR ($CDCl_3$, 298 K) spectrum of the crude reaction mixture after 2 hours. (*) 1,2-dichloroethane (0.25 equivalents) as internal standard.

Hydrosilylation of cis-2-octene using Ph_3SiH (Table 1, entry 4)

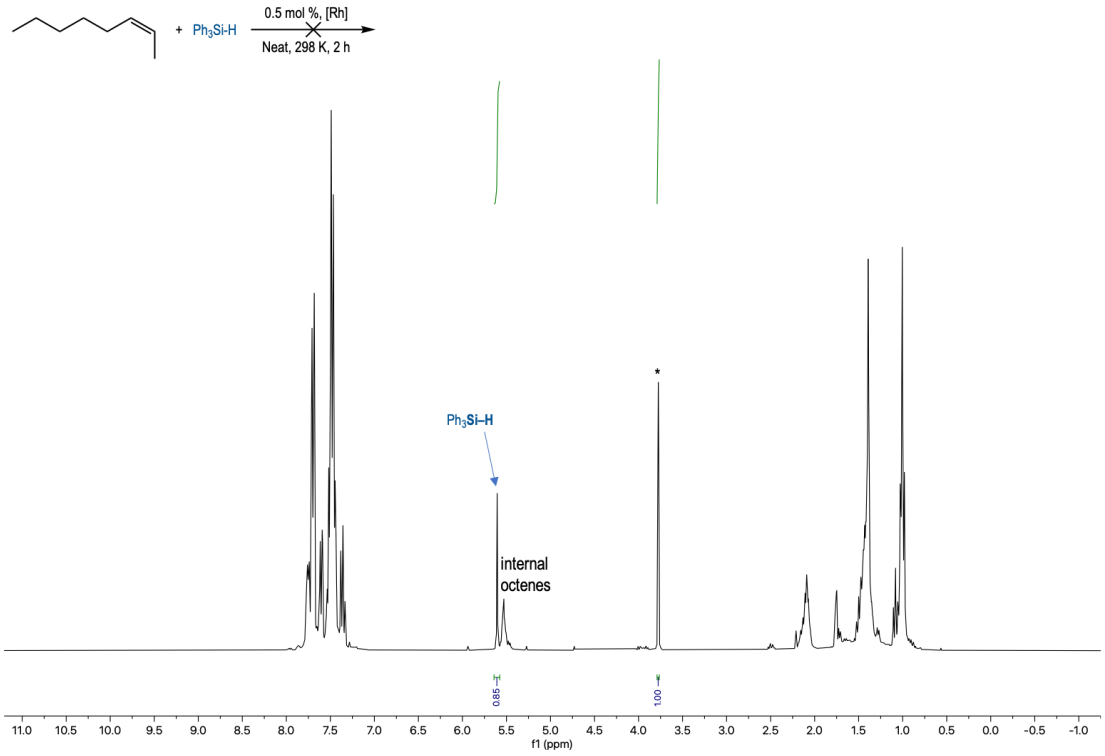


Figure S.6. ^1H NMR ($CDCl_3$, 298 K) spectrum of the crude reaction mixture after 2 hours. (*) 1,2-dichloroethane (0.25 equivalents) as internal standard.

Hydrosilylation of 1-octene using Ph_2SiH_2 (Table 1, entry 5)

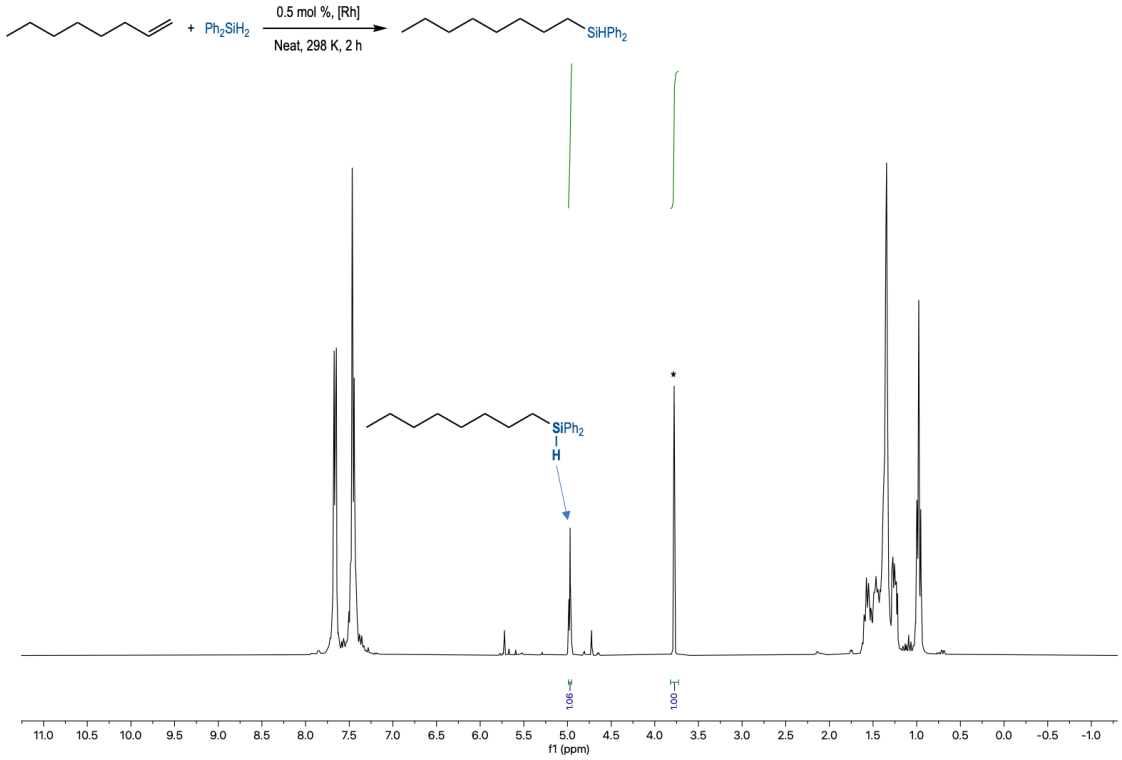


Figure S.7. ^1H NMR ($CDCl_3$, 298 K) spectrum of the crude reaction mixture after 2 hours. (*) 1,2-dichloroethane (0.25 equivalents) as internal standard.

Hydrosilylation of cis-2-octene using Ph_2SiH_2 (Table 1, entry 6)

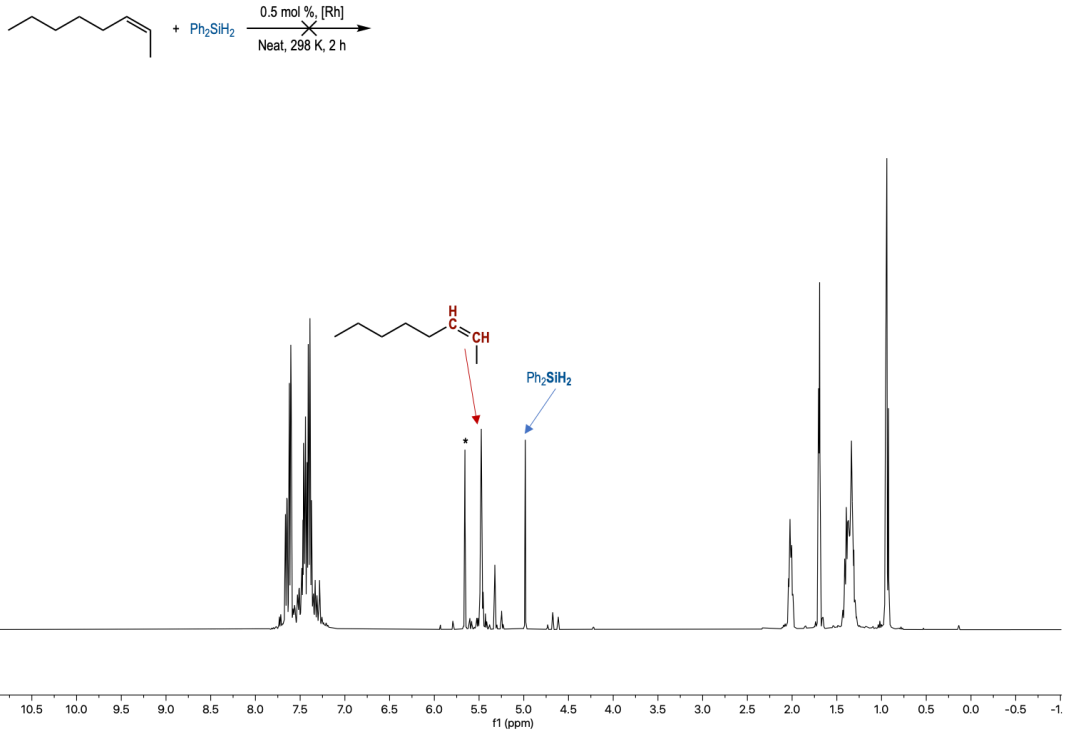


Figure S.8. ^1H NMR ($CDCl_3$, 298 K) spectrum of the crude reaction mixture after 2 hours. (*) Siloxanes formed by reaction of some remaining diphenylsilane with water.

3. Reaction of ethyl acetate with Et_3SiH, Ph_3SiH and Ph_2SiH_2 using [Rh(SiS^{i}Bu)] as catalyst.

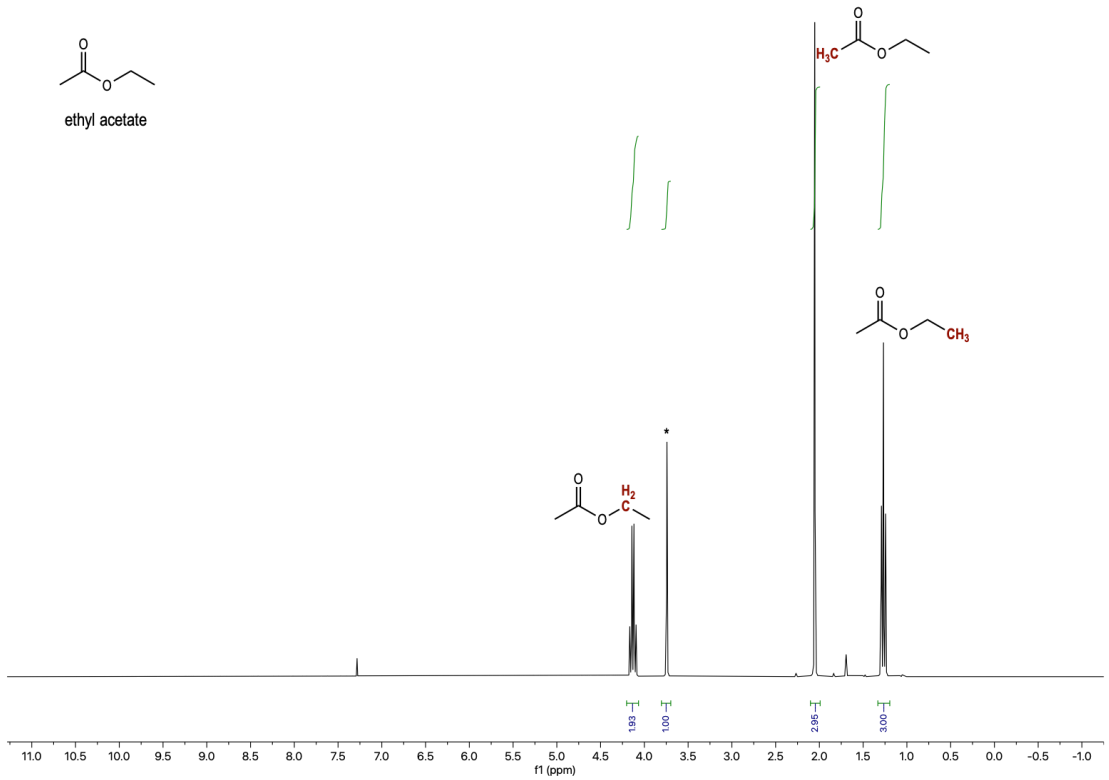


Figure S.9. ^1H NMR ($CDCl_3$, 298 K) spectrum of ethyl acetate. (*) 1,2-dichloroethane (0.25 equivalents) as internal standard.

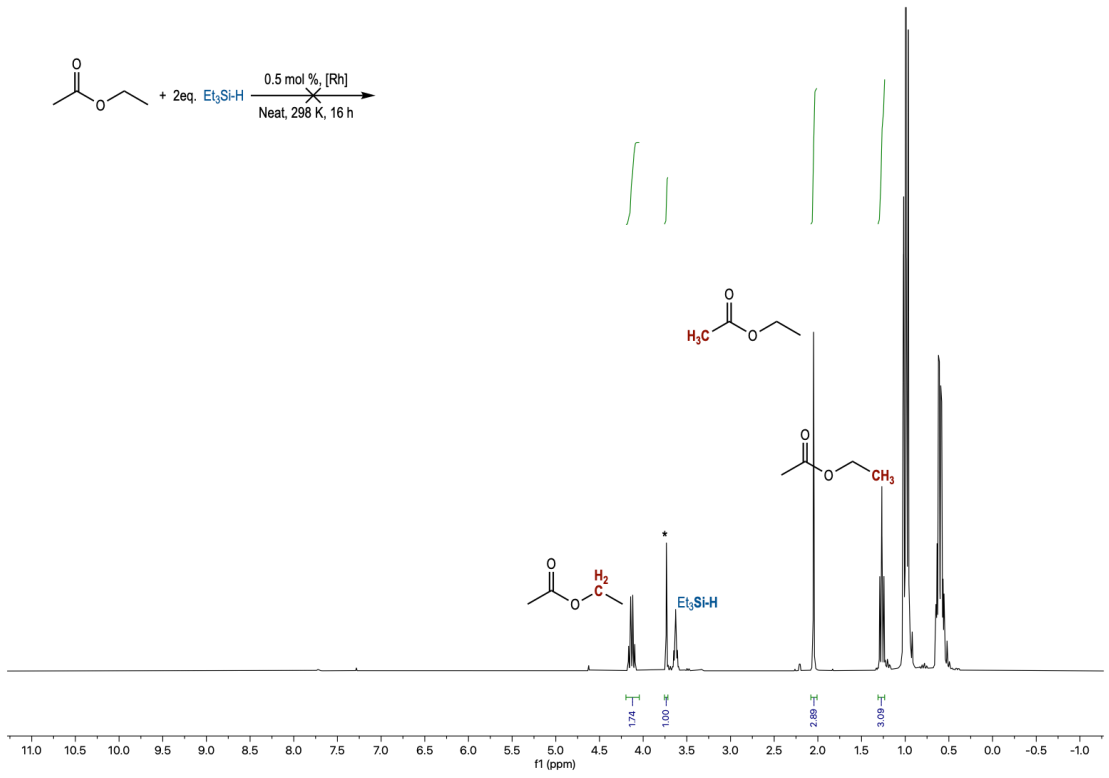


Figure S.10. ^1H NMR ($CDCl_3$, 298 K) spectrum of the crude reaction mixture after 16 hours. (*) 1,2-dichloroethane (0.25 equivalents) as internal standard.

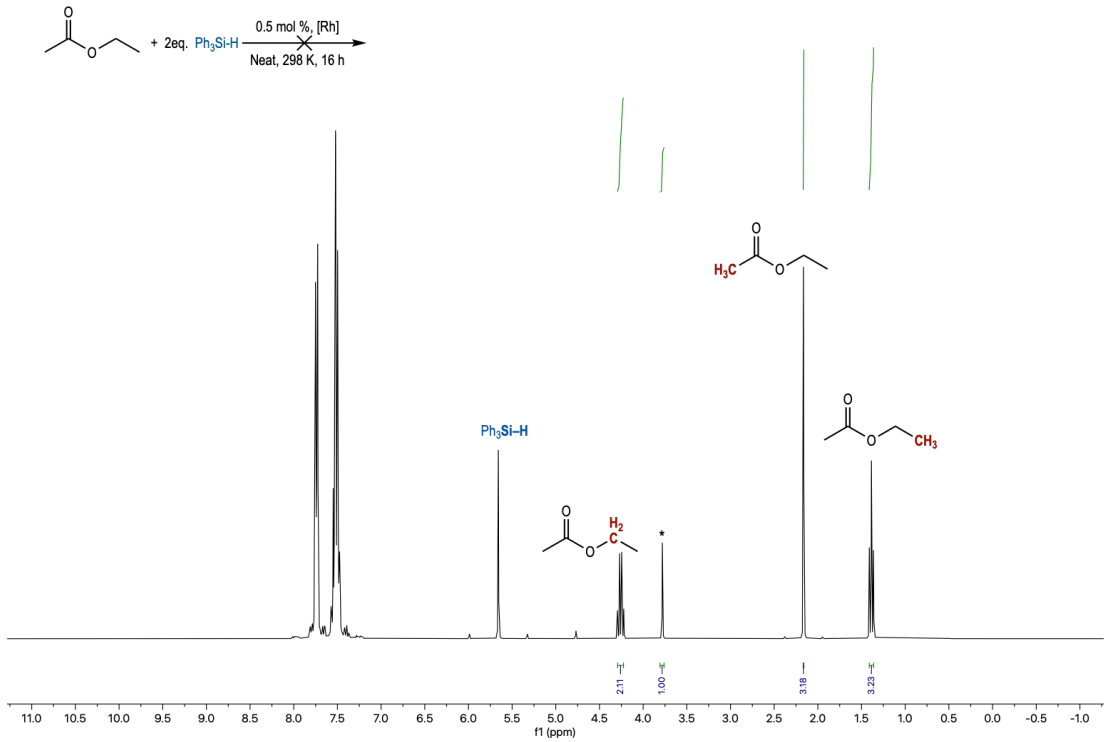


Figure S.11. ^{1}H NMR ($CDCl_3$, 298 K) spectrum of the crude reaction mixture after 16 hours. (*) 1,2-dichloroethane (0.25 equivalents) as internal standard.

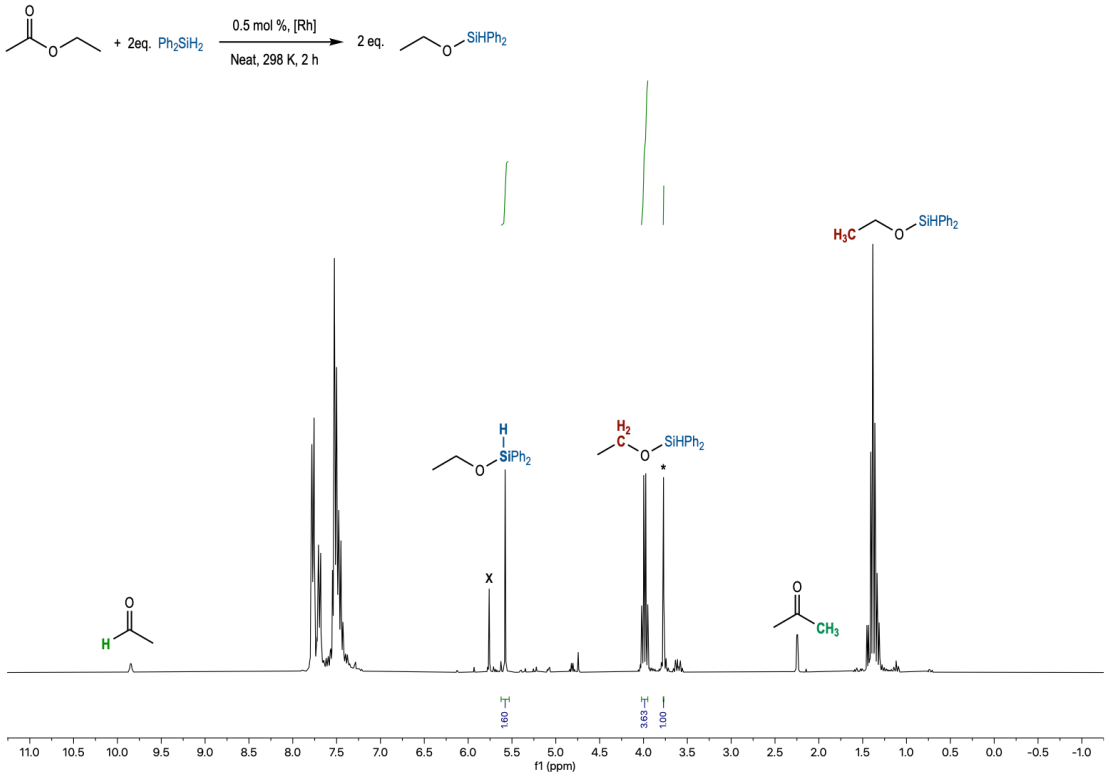


Figure S.12. ^{1}H NMR ($CDCl_3$, 298 K) spectrum of the crude reaction mixture after 16 hours. (*) 1,2-dichloroethane (0.25 equivalents) as internal standard. (x) Siloxanes formed by reaction of some remaining diphenylsilane with water.

4. Reaction of methyl 5-hexenoate with Et_3SiH and Ph_2SiH_2 using [Rh(SiS^{i}Bu)] as catalyst.

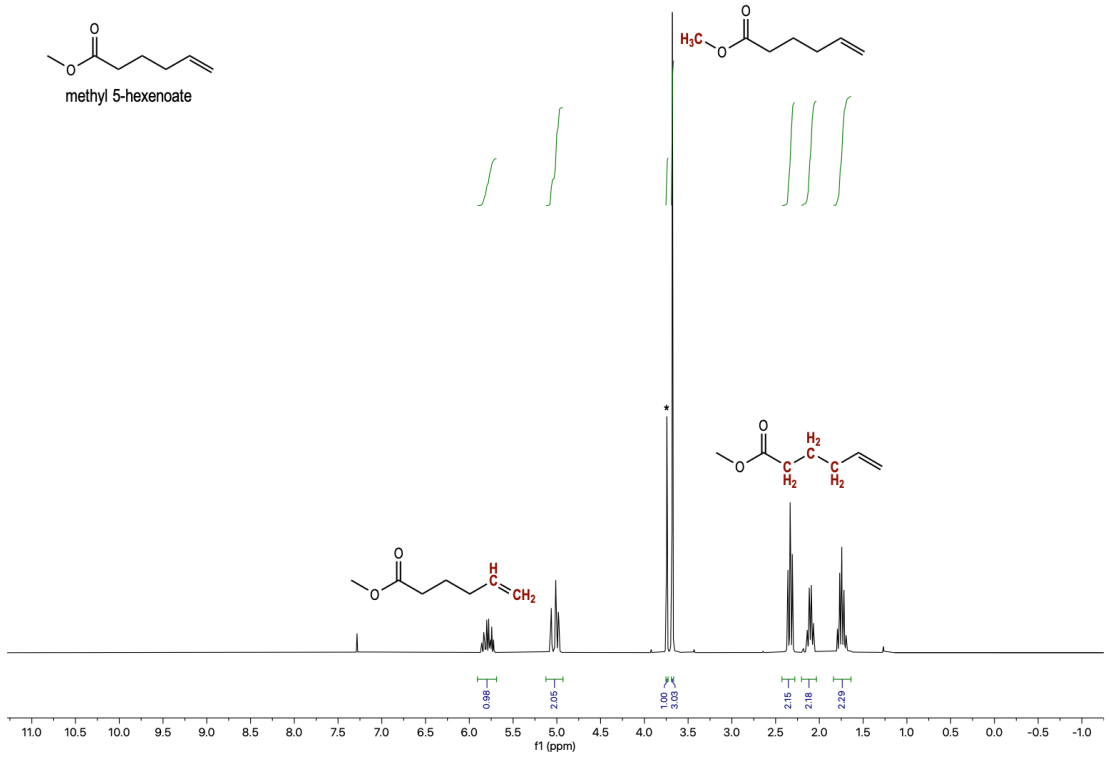


Figure S.13. ^{1}H NMR ($CDCl_3$, 298 K) spectrum of methyl 5-hexenoate. (*) 1,2-dichloroethane (0.25 equivalents) as internal standard.

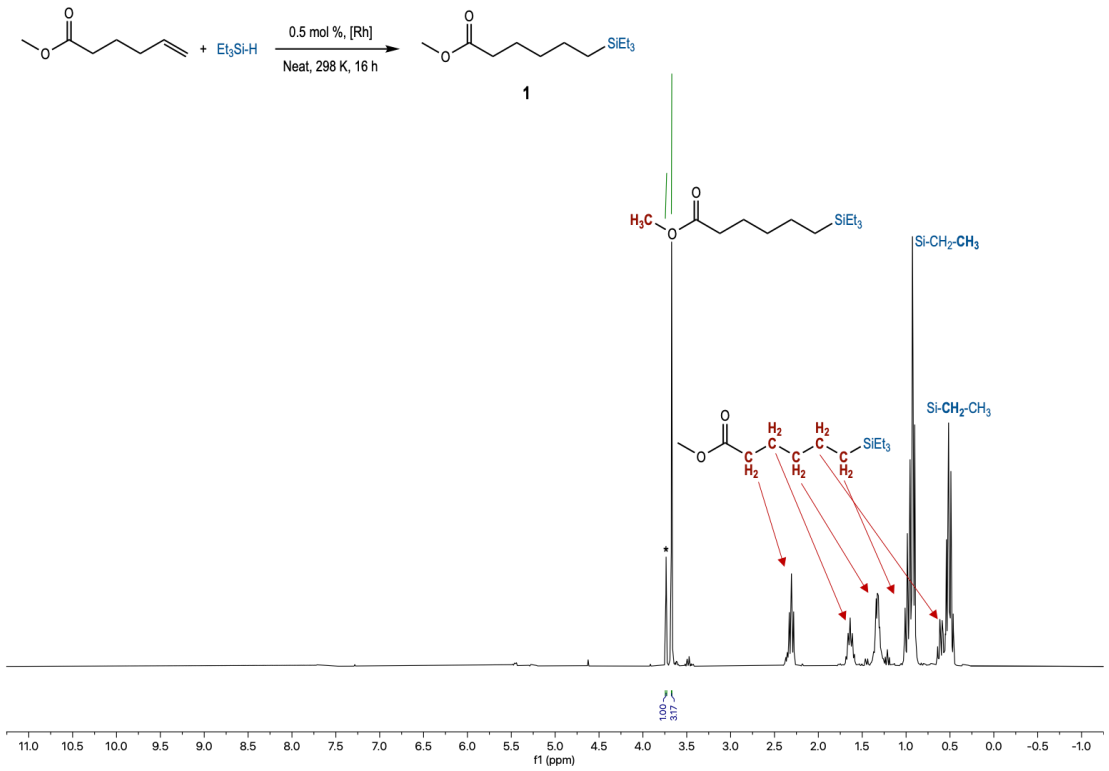


Figure S.14. ^{1}H NMR ($CDCl_3$, 298 K) spectrum of the crude reaction mixture after 16 hours. (*) 1,2-dichloroethane (0.25 equivalents) as internal standard.

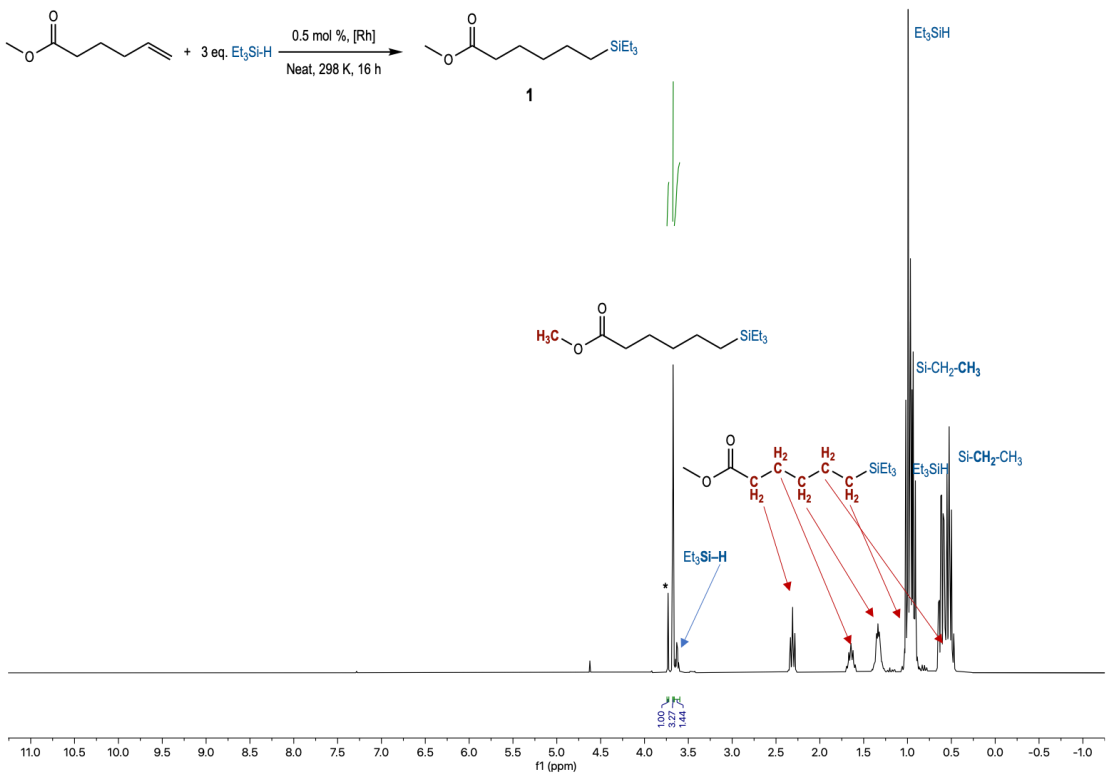


Figure S.15. ^{1}H NMR ($CDCl_3$, 298 K) spectrum of the crude reaction mixture after 16 hours. (*) 1,2-dichloroethane (0.25 equivalents) as internal standard.

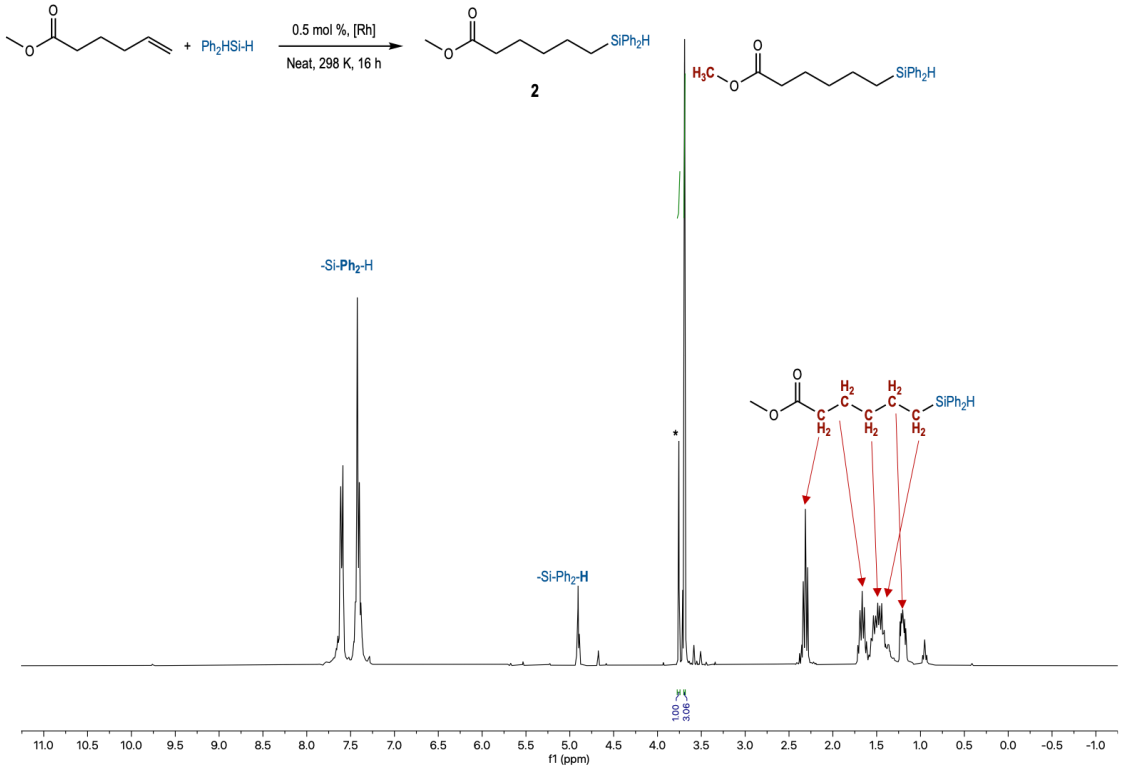


Figure S.16. ^{1}H NMR ($CDCl_3$, 298 K) spectrum of the crude reaction mixture after 16 hours. (*) 1,2-dichloroethane (0.25 equivalents) as internal standard.

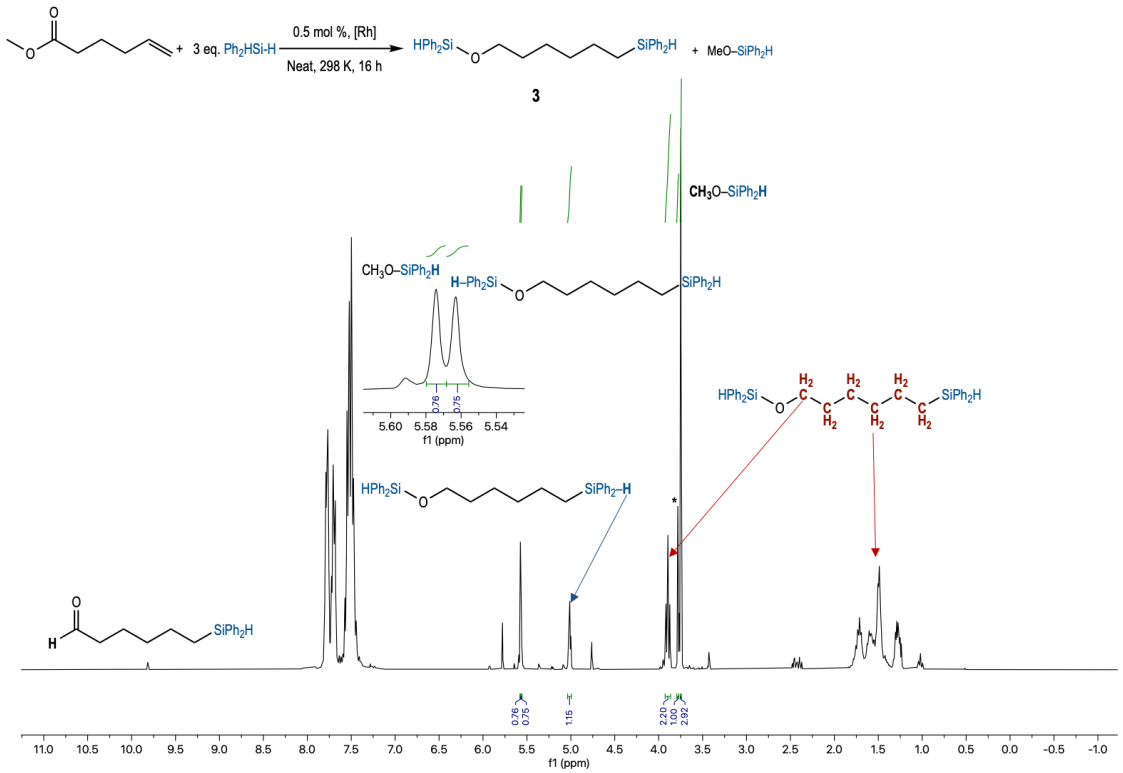


Figure S.17. ^{1}H NMR ($CDCl_3$, 298 K) spectrum of the crude reaction mixture after 16 hours. (*) 1,2-dichloroethane (0.25 equivalents) as internal standard.

5. Reaction of ethyl oleate with Et_3SiH and Ph_2SiH_2 using [Rh(SiS^{i}Bu)] as catalyst.

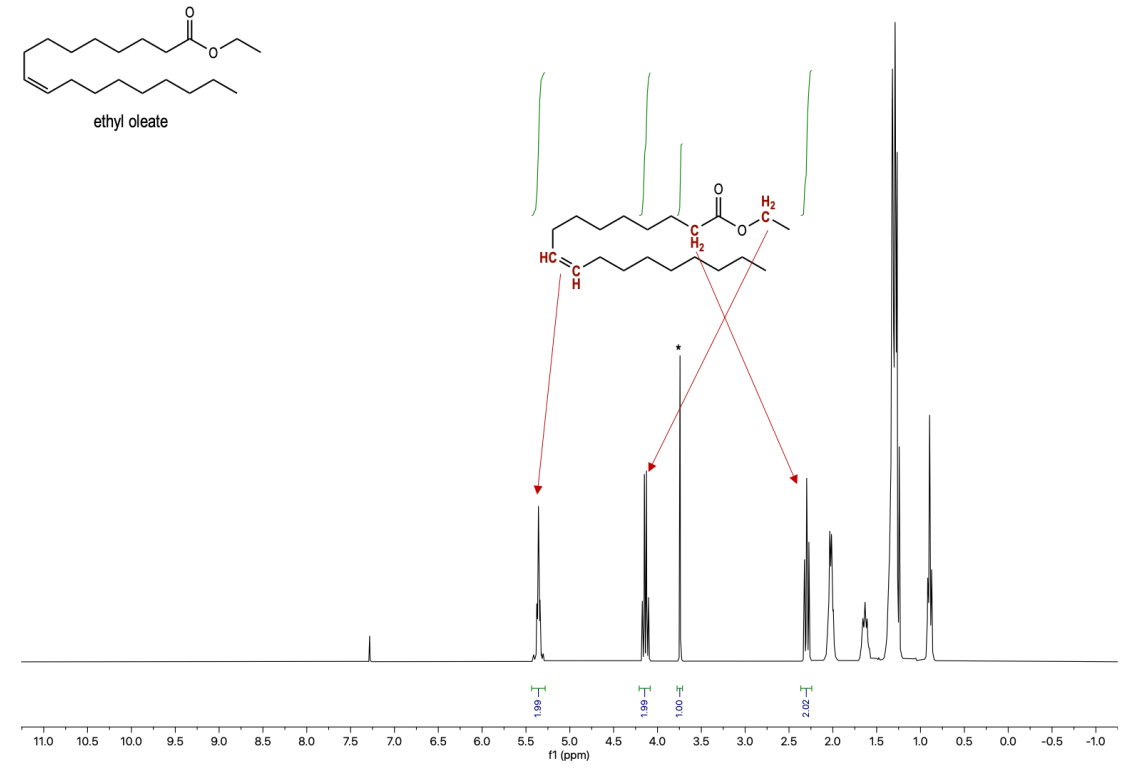


Figure S.18. ^{1}H NMR ($CDCl_3$, 298 K) spectrum of ethyl oleate. (*) 1,2-dichloroethane (0.25 equivalents) as internal standard.

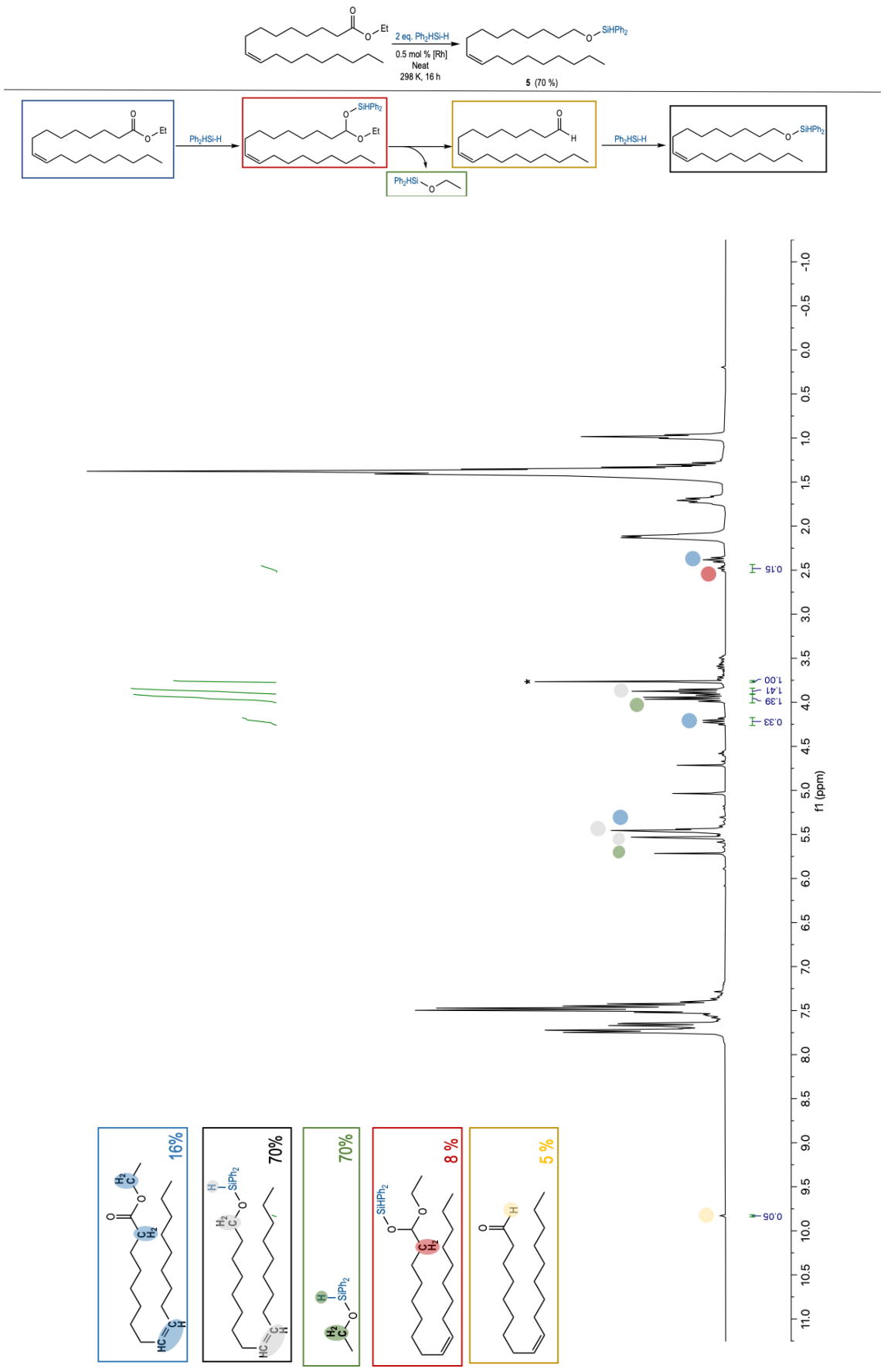


Figure S.19. ^{1}H NMR ($CDCl_3$, 298 K) spectrum of the crude reaction mixture after 16 hours. (*) 1,2-dichloroethane (0.25 equivalents) as internal standard.

6. Reaction of olive oil with Ph_2SiH_2 using [Rh(SiS^{i}Bu)] as catalyst.

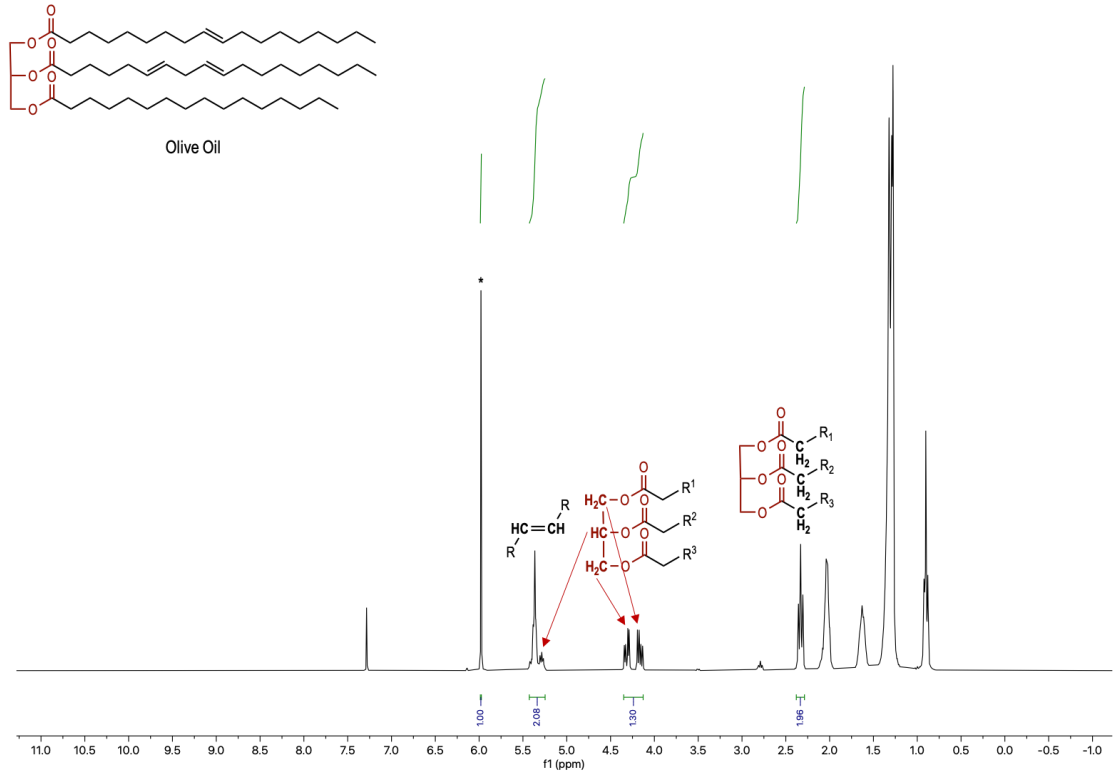


Figure S.20. ^{1}H NMR ($CDCl_3$, 298 K) spectrum of olive oil. (*) tetrachloroethane (0.5 equivalents by fatty ester chain) as internal standard.

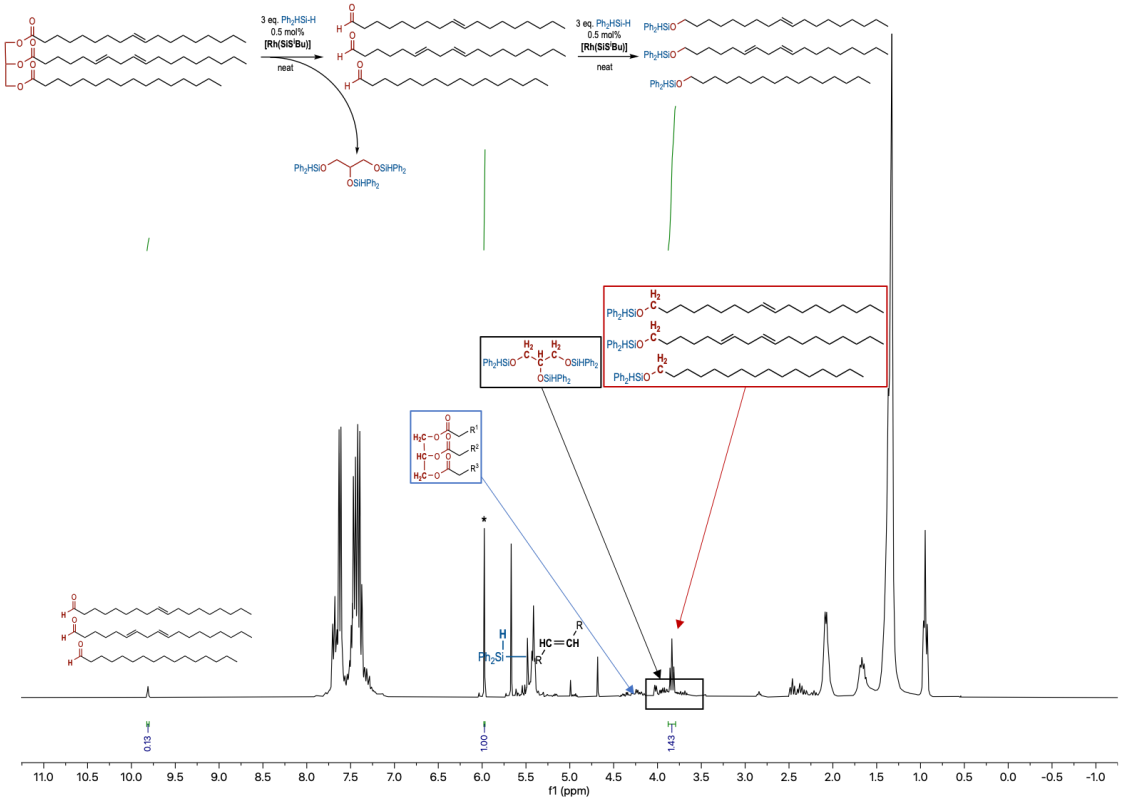


Figure S.21. ^{1}H NMR ($CDCl_3$, 298 K) spectrum of the crude reaction mixture after 16 hours. (*) tetrachloroethane (0.5 equivalents by fatty ester chain) as internal standard.

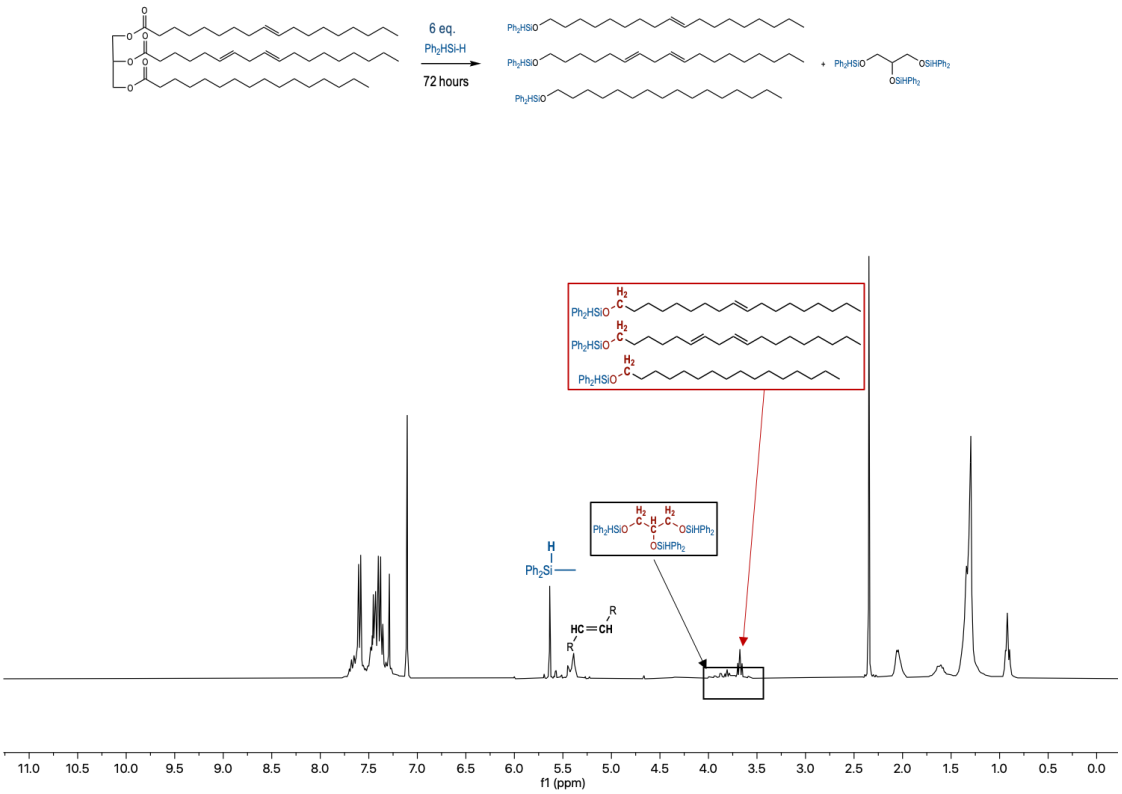


Figure S.22. ^{1}H NMR ($CDCl_3$, 298 K) spectrum of the crude reaction mixture after 72 hours.

- Hydrolysis of silyl ethers: Synthesis of fatty alcohols

Hydrolysis of the silyl ethers was carried out using an excess of NaOH (100 mg NaOH per 100 mg reaction mixture) in a 1:1 mixture of MeOH:CH_2Cl_2 (1mL:1mL). After one hour, the solvents were removed, the reaction crude redisolved in $CHCl_3$ (10 mL) and washed with water (3 x 10 mL). The organic layer was dried with MgSO4 and evaporated to obtain the fatty alcohols.

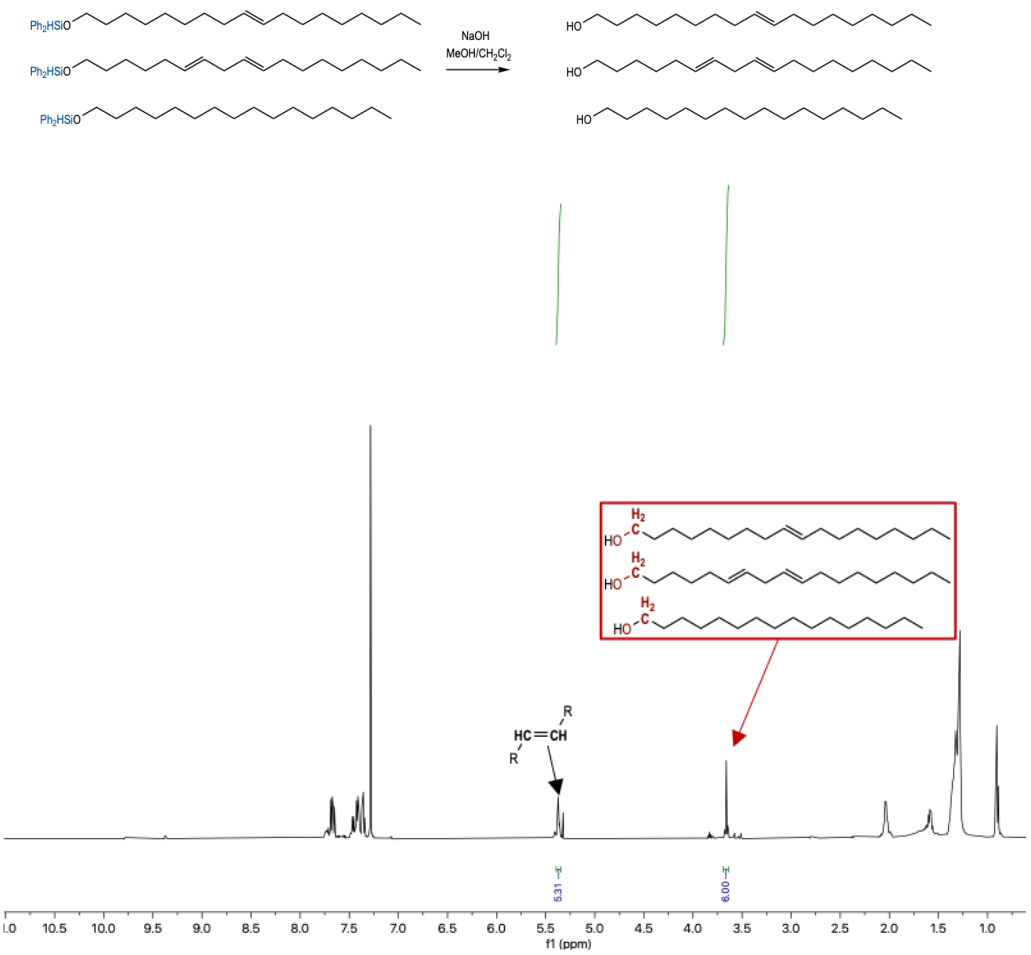


Figure S.23. ^{1}H NMR ($CDCl_3$, 298 K) spectrum of the crude reaction mixture (reduction of olive oil) after 72 hours and after hydrolysis reaction (1h).

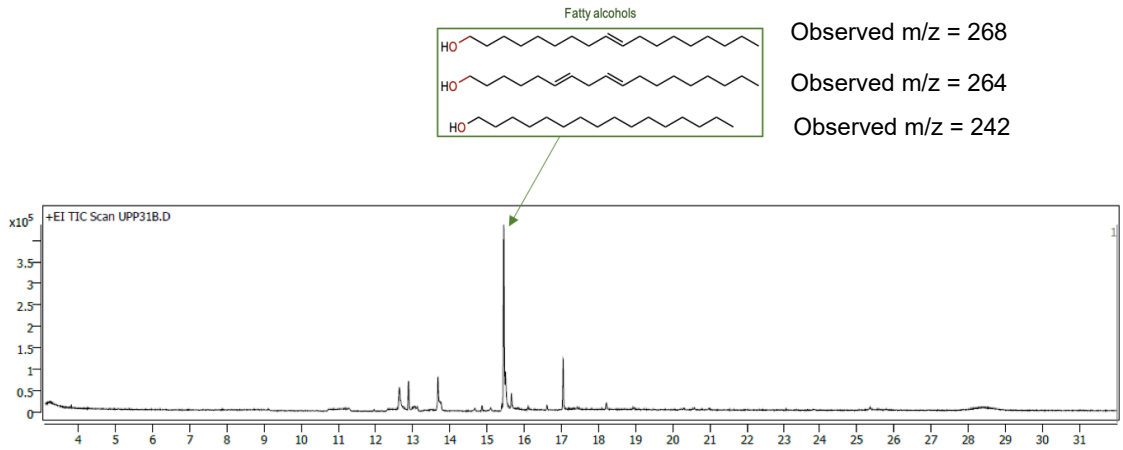


Figure S.24. GC-MS of hydrolysis reaction.

7. Reaction of other plant oils with Ph_2SiH_2 using [Rh(SiS^{i}Bu)] as catalyst.

- Coconut Oil

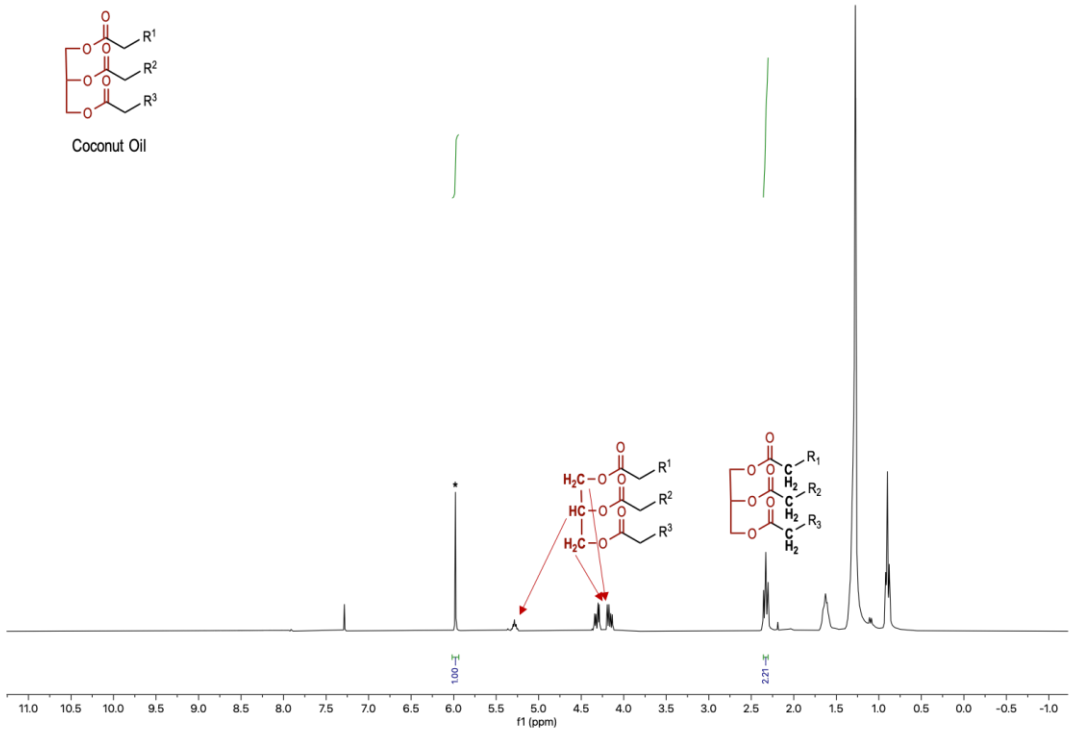


Figure S.25. ^{1}H NMR ($CDCl_3$, 298 K) spectrum of coconut oil. (*) tetrachloroethane (0.5 equivalents by fatty ester chain) as internal standard.

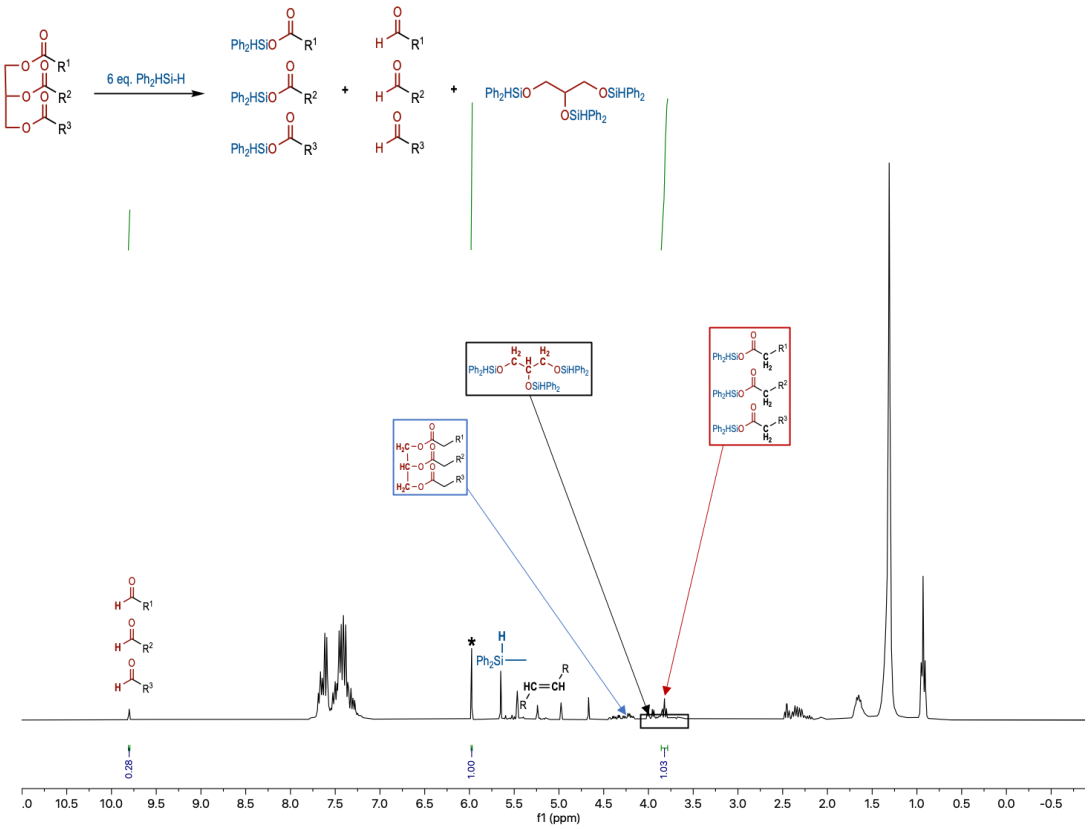


Figure S.26. ^{1}H NMR ($CDCl_3$, 298 K) spectrum of the crude reaction mixture after 16 hours of reaction of coconut oil with diphenylsilane. (*) tetrachloroethane (0.5 equivalents by fatty ester chain) as an internal standard.

- Castor Oil

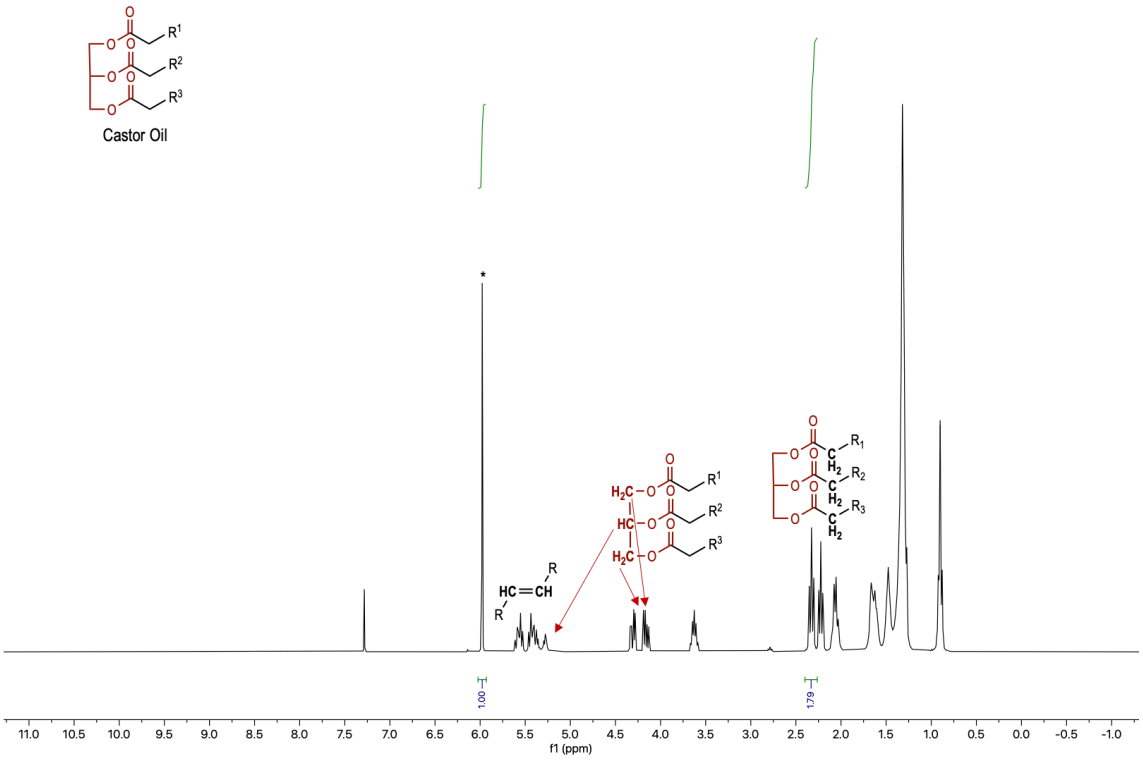


Figure S.27. ^{1}H NMR ($CDCl_3$, 298 K) spectrum of castor oil. (*) tetrachloroethane (0.5 equivalents by fatty ester chain) as internal standard.

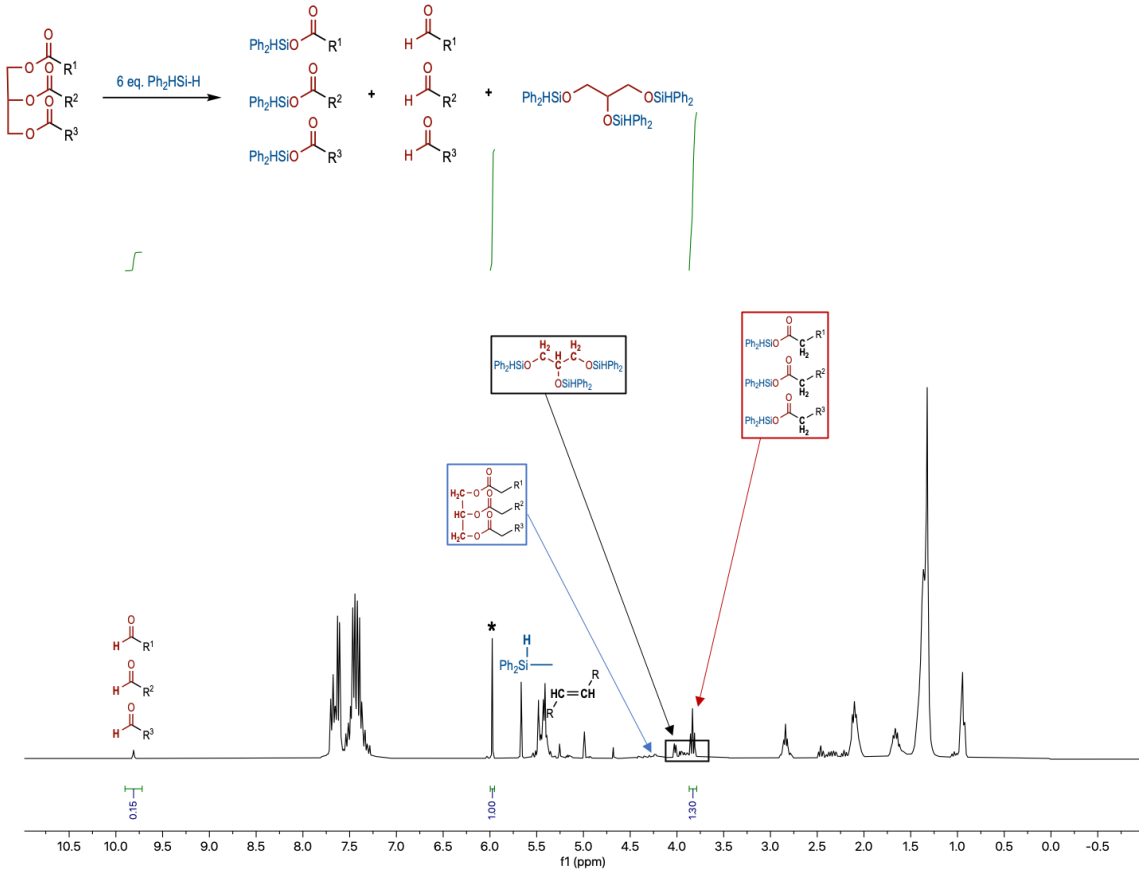


Figure S.28. ^{1}H NMR ($CDCl_3$, 298 K) spectrum of the crude reaction mixture after 16 hours of reaction of castor oil with diphenylsilane. (*) tetrachloroethane (0.5 equivalents by fatty ester chain) as an internal standard.

- Sesame Oil

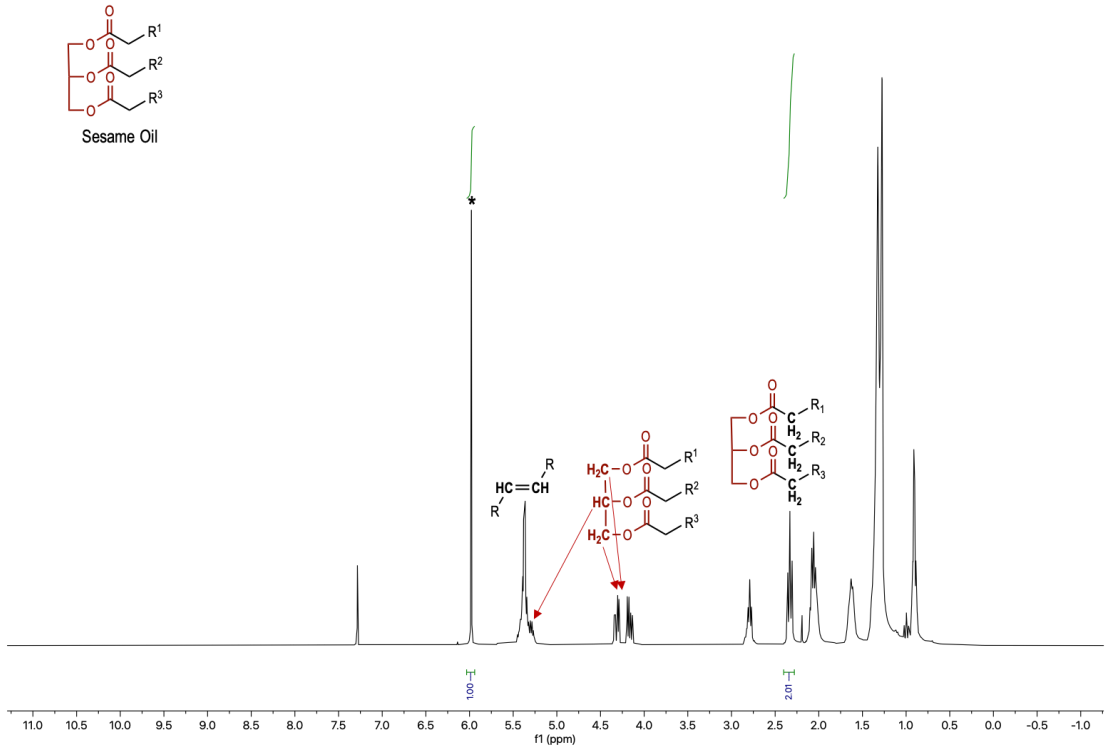


Figure S.29. ^{1}H NMR ($CDCl_3$, 298 K) spectrum of sesame oil. (*) tetrachloroethane (0.5 equivalents by fatty ester chain) as internal standard.

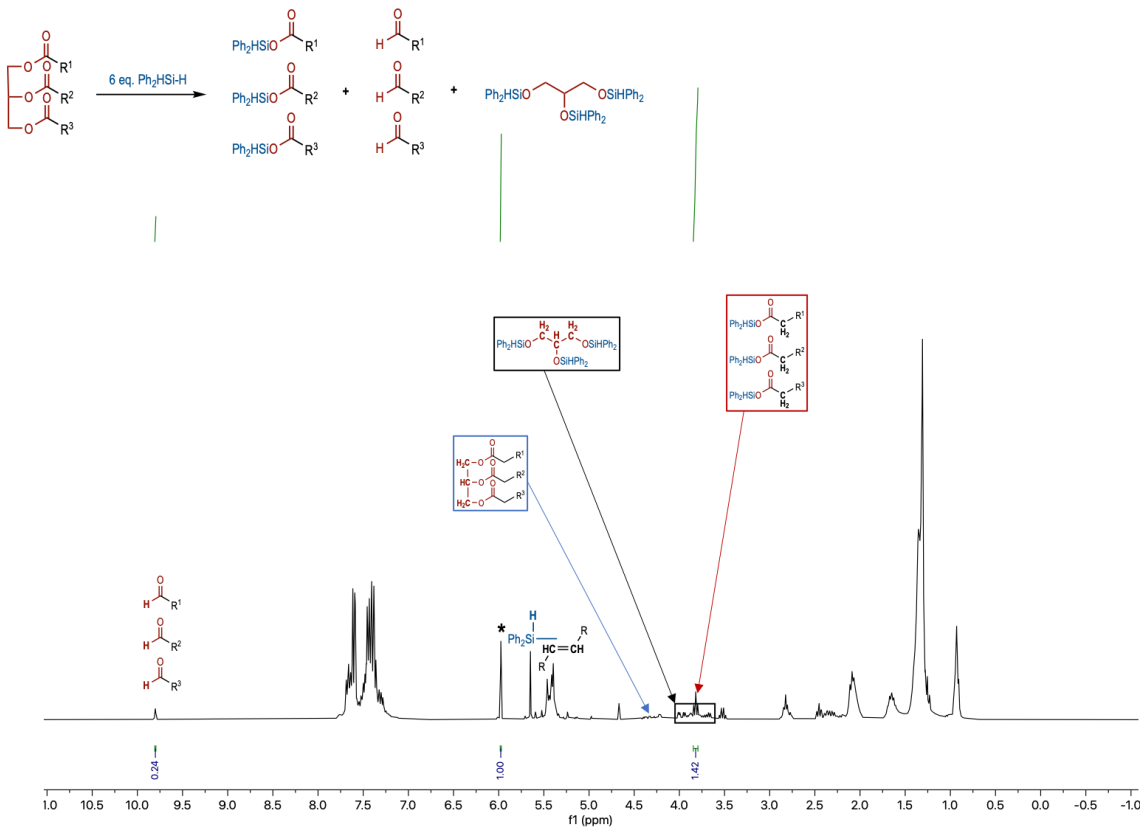


Figure S.30. ^{1}H NMR ($CDCl_3$, 298 K) spectrum of the crude reaction mixture after 16 hours of reaction of sesame oil with diphenylsilane. (*) tetrachloroethane (0.5 equivalents by fatty ester chain) as an internal standard.

- Sunflower Oil

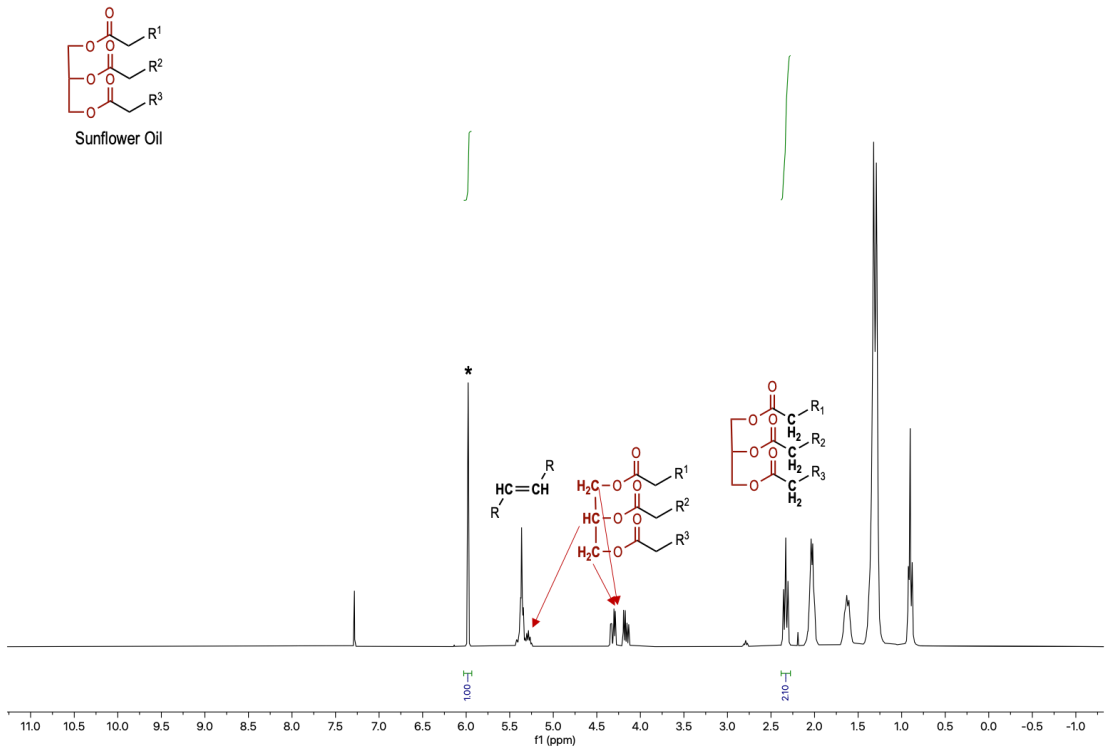


Figure S.31. ^{1}H NMR ($CDCl_3$, 298 K) spectrum of sunflower oil. (*) tetrachloroethane (0.5 equivalents by fatty ester chain) as internal standard.

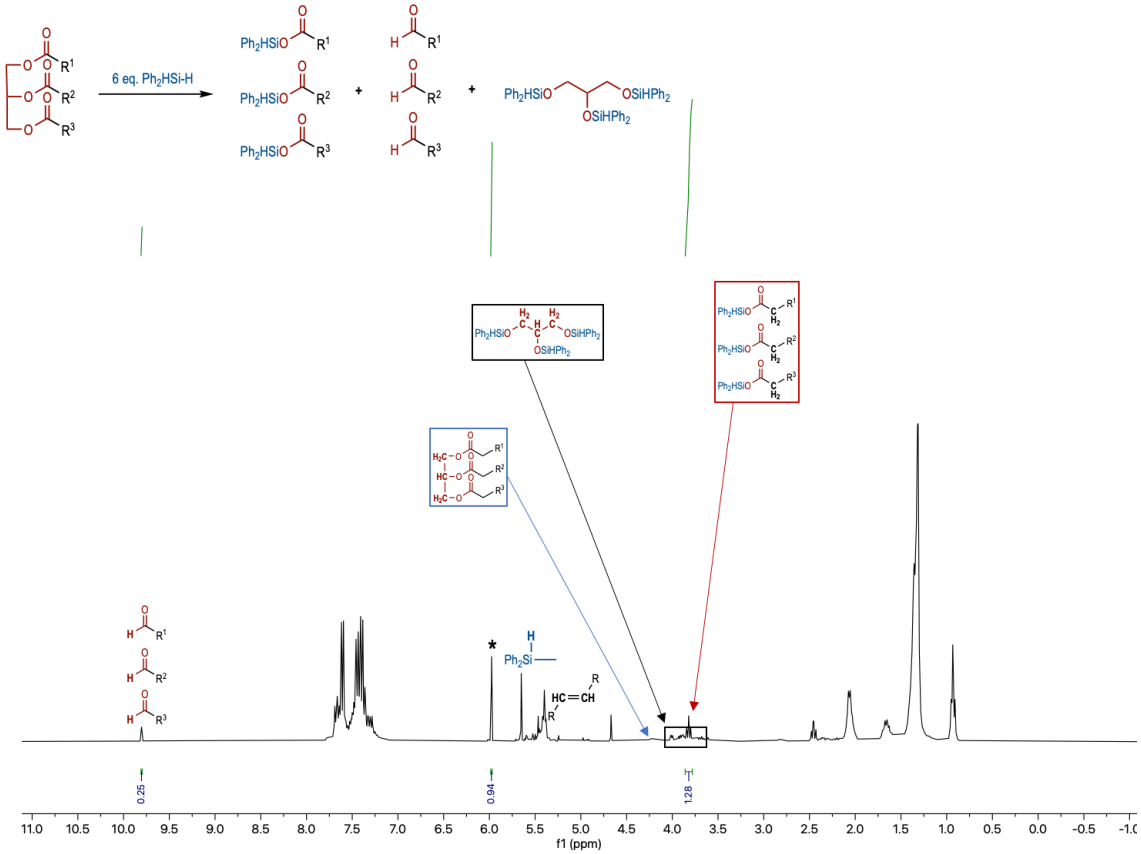


Figure S.32. ^{1}H NMR ($CDCl_3$, 298 K) spectrum of the crude reaction mixture after 16 hours of reaction of sunflower oil with diphenylsilane. (*) tetrachloroethane (0.5 equivalents by fatty ester chain) as an internal standard.

Attempt of the recovery of the rhodium complex: The reduction of olive oil was conducted as per the method described in Table 2, entry 1. After 24 hours of reaction, 1 mL of hexane was added to the reaction mixture, ultrasonicated, centrifuged and the liquid was separated from a deposited solid. It was presumed that the yellow colored liquid obtained upon centrifuge contained catalyst. However, its re-use as a catalyst in the further reduction of olive oild did not lead to the formation on any fatty alcohols.

8. References

1. U. Prieto, S. Azpeitia, E. San Sebastian, Z. Freixa, M. A. Garralda and M. A. Huertos, *ChemCatChem*, 2021, **13**, 1403