Supporting Information

Photochemical Organocatalytic Regio- and Enantioselective Conjugate Addition of Allyl Groups to Enals

Martin Berger, Davide Carboni, and Paolo Melchiorre*

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Author Contributions

M.B. Conceptualization: Equal; Methodology: Lead; Writing – original draft: Lead; Writing – review & editing: Supporting
D.C. Investigation: Supporting; Methodology: Supporting
P.M. Conceptualization: Equal; Funding acquisition: Lead; Writing – original draft: Supporting; Writing – review & editing: Lead.
1 General Information

The NMR spectra were recorded at 300 MHz, 400 MHz and 500 MHz spectrometers for $^1$H or at 75 MHz, 101 MHz and 126 MHz for $^{13}$C or 376 MHz for $^{19}$F, respectively. The chemical shifts (δ) for $^1$H and $^{13}$C signals are given in ppm relative to residual signals of the solvents (CHCl$_3$ at 7.26 ppm in $^1$H NMR and at 77.16 ppm in $^{13}$C NMR spectra). Coupling constants are given in Hz. The following abbreviations are used to indicate the multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (heptet), m (multiplet), br (broad).

High-resolution mass spectra (HRMS) were obtained from the ICIQ High-Resolution Mass Spectrometry Unit on MicroTOF Focus and Maxis Impact (Bruker Daltonics) with electrospray ionization or atmospheric pressure chemical ionization. X-ray data were obtained from the ICIQ X-Ray Unit using a Bruker-Nonius diffractometer equipped with an APPEX 2 4K CCD area detector. Optical rotations were measured on a Polarimeter Jasco P-1030 and are reported as follows: $[\alpha]_D$ ambient temperature (c in g per 100 mL, solvent). Cyclic voltammetry studies were carried out on a Princeton Applied Research PARSTAT 2273 potentiostat, offering compliance voltage up to ± 100 V (available at the counter electrode), ± 10 V scan range and ± 2 A current range. UV-Vis measurements were carried out on a Shimadzu UV-2401PC spectrophotometer equipped with photomultiplier detector, double beam optics and D2 and W light sources.

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General Procedures. All reactions were set up under an argon atmosphere in dry glassware using standard Schlenk techniques, unless otherwise stated. Synthesis grade solvents were used as purchased. Anhydrous solvents were taken from a commercial SPS solvent dispenser. Chromatographic purification of products was accomplished using flash column chromatography (FC) on silica gel (35-70 mesh). For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF$_{254}$, 0.25 mm) were used, using UV light as the visualizing agent and basic aqueous potassium permanganate (KMnO$_4$) as developing agents. Organic solvents were removed under reduced pressure on a Büchi rotary evaporator.

Determination of Regioisomeric Ratio. The regioisomeric ratio was determined by $^1$H NMR analysis of the clean products through integration of diagnostic signals. The obtained values were found fully comparable to the regioisomeric ratio when determined from the $^1$H NMR spectra of the individual crude reaction mixtures after work-up, indicating that linear and branched isomers are completely inseparable. However, due to overlapping minor impurities in the spectra of some crude mixtures, the most reliable results were gathered by analysis of the purified products.

Determination of Enantiomeric Purity: UPC$^2$ analysis on chiral stationary phase was performed on a Waters ACQUITY® instrument using IA-3, ID-3, IE-3, IG-3 and OJ-3 chiral columns. The exact conditions for the analyses are specified in the experimental section of the individual compounds. UPC$^2$ traces were compared to racemic samples prepared by running the reaction either in the presence of a catalytic amount (20 mol%) of an approximately 1:1 mixture of R- and S- catalyst A or an approximately 1:1 mixture of (2R,5R)- and (2S,5S)-catalyst C, the latter being commercially available from Sigma Aldrich.

Materials: Commercial grade reagents and solvents were purchased at the highest commercial quality from Sigma Aldrich, Fluka, Acros Organics, Fluorochem or Alfa Aesar and used as received unless otherwise stated. The chiral secondary amine catalyst A was prepared according to the reported literature by our group. Some of the enal substrates (1), including 4-nitrocinnamaldehyde 1c, 4-bromocinnamaldehyde 1f and 4-chlorocinnamaldehyde 1e, are commercially available and were used as received. Cinnamaldehyde 1a is commercially available.
and was distilled prior to use. Other enals and allyl silanes were prepared according to the literature, as detailed in the experimental section.

2 Unsuccessful substrates

The following substrates offered unsatisfactory results:

Unsuccessful substrates

![Figure S1. Unsuccessful and low-yielding substrates; reactions performed under the optimized conditions]

3 Unsuccessful reactions with aliphatic enals

Direct excitation of aliphatic enals: We attempted the conjugate allylation of octenal and 4,4-dimethyl-2-pentenal (which cannot undergo tautomerization to the dienamine) under the optimized conditions but with irradiation at 365 nm (110 mW/cm$^2$). However, no product was obtained.

Unsuccessful reactions with aliphatic enals

![Figure S2. Unsuccessful conjugate allylation of aliphatic enals by direct excitation.]

We also attempted the conjugate allylation of octenal using an external photocatalyst to generate the allyl radical from 2b. However, no product was obtained.

Unsuccessful conjugate allylation of octenal in the presence of an external photocatalyst.

![Figure S3. Unsuccessful conjugate allylation of octenal in the presence of an external photocatalyst.]

S4
4 Experimental section

4.1 Preparation of enals 1

Some enals 1 were prepared using procedures previously reported in the literature. Figure S4 depicts the synthesized enals providing the corresponding references.

![Enal structures](image)

Figure S4. Enals synthesized according to procedures reported in the literature

4.2 Synthesis of allyl silanes 2

For the preparation of allylic silanes 2, various synthetic sequences were followed:

**Sequence A:** Silane 2a was prepared in 2 steps, starting from commercially available alcohol A-a via trifluoroacetic esters T-a, applying conditions adapted from Woo et al.\[4\]

**Sequence B:** Silanes 2d and 2e were synthesized in 3 steps, starting from commercially available ketones K-d,e via alcohols A-d,e and via trifluoroacetic esters T-d,e, applying conditions adapted from Woo et al.\[4\]

\[ d: R = cyclohexyl \]
\[ e: R = isopropyl \]
Note - The conversion of alcohols A-d,e to their trifluoroacetic esters afforded the linear products T-d,e instead of the expected branched products. We think that this is attributed to the instability of the branched isomers, which likely undergo allylic isomerization under ambient conditions.

Sequence C: Allyl silanes 2b, 2c, 2f, 2g, 2h were synthesized in 2 steps from alcohols A-b,c,f,g,h with conditions adapted from Szabó et al.[5] and the alcohols were prepared from commercially available ketones K-b,c,f,g,h with conditions adapted from Woo et al.[4]

General procedure A for the synthesis of allylic alcohols (A-b,c,d,e,f,g,h)
To a dry round bottom flask, the corresponding ketone K-b,c,d,e,f,g,h (1.0 equiv.) was added as solution in dry THF (0.5 M) under an argon atmosphere. After cooling to 0 °C, a solution of vinyl magnesium bromide (1.0 M in THF, 1.3 equiv.) was added dropwise. The reaction mixture was stirred at RT overnight. The solution was then quenched with a saturated solution of NH₄Cl, diluted with EtOAc and extracted three times with EtOAc. The combined organic layers were dried over MgSO₄, filtered and concentrated under reduced pressure. The crude alcohols were purified by column chromatography on silica gel to afford the desired allylic alcohols A-b,c,d,e,f,g,h.

General procedure B for the synthesis of trifluoroacetic esters (T-a,d,e)
A dry round bottom flask was charged with a solution of the allylic alcohol A-a,d,e (1 equiv.), triethylamine (1.0 equiv.) and 4-(dimethylamino)pyridine (0.08 equiv.) in CH₂Cl₂ (anhydrous). After cooling to 0 °C, trifluoroacetic anhydride (1.0 equiv.) was added. After stirring for 2 h at 0 °C, the mixture was stirred at RT overnight. The reaction mixture was quenched with water and the organic layer was separated. The aqueous phase was extracted three times with CH₂Cl₂ and the combined organic layers were dried with MgSO₄ and filtered. Concentration under reduced pressure and purification by column chromatography on silica gel afforded the desired products T-a,d,e.

General procedure C for the synthesis of allyl silanes from trifluoroacetic esters (2a,d,e)
In a dry round bottom flask, a solution of trifluoroacetic ester T-a,d,e (1.0 equiv.), hexamethyldisilane (1.0 equiv.) and Pd(dba)₂ (20 mol%) in THF (anhydrous) was stirred for 3 days at RT under an argon atmosphere. The crude mixture was then filtered through a pad of silica gel with pentane in order to remove most of the palladium salts. The filtrate was concentrated in vacuo (800 mbar) and the residual oil was purified by column chromatography (gravity protocol) on silica gel to afford the desired allyl silane 2a,d,e.

General procedure D for the synthesis of allyl silanes from alcohols (2b,c,f,g,h)
In a flame dried and argon purged round bottom flask, the corresponding allylic alcohol A-b,c,f,g,h (1 eq.) was dissolved in a 1:1 mixture of methanol and DMSO (both anhydrous). Hexamethyldisilane (1.2 eq) and Pd(OCOCF₃)₂ (5-6 mol%) were added and the reaction mixture was stirred for 18 hours at 60 °C. The crude mixture was extracted three times with pentane, the combined organic layers were dried over MgSO₄ and concentrated in vacuo. The product was
purified by column chromatography (gravity protocol) on silica gel to give the desired allyl silane 2b,c,f,g,h.

4.2.1 Characterization of allylic alcohols (A-b-h)

1-Vinylcyclohexan-1-ol (A-b)
Prepared according to procedure A described above using cyclohexanone K-b (1.0 equiv., 3.00 mmol, 294.0 mg, 0.31 mL), THF (anhydrous, 6.00 mL) and vinyl magnesium bromide (1.0 M solution in THF, 1.3 equiv., 3.9 mmol, 3.90 mL). The crude product was purified by flash chromatography (silica gel, 90:10 hexanes:EtOAc) to afford the product as a colorless liquid (246.0 mg, 65% yield). Analytical data was found to be in agreement with the literature.[6]

1H NMR (400 MHz, CDCl3); δ = 5.98 (dd, J = 17.4, 10.8 Hz, 1H), 5.25 (dd, J = 17.4, 1.3 Hz, 1H), 5.04 (dd, J = 10.8, 1.3 Hz, 1H), 1.77 – 1.16 (m, 10H) ppm.

4-Vinyltetrahydro-2H-pyran-4-ol (A-c)
Prepared according to procedure A described above using tetrahydro-4H-pyran-4-one K-c (1.0 equiv., 6.00 mmol, 600.7 mg, 554 μL), THF (anhydrous, 12.0 mL) and vinyl magnesium bromide (1.0 M solution in THF, 1.5 equiv., 9.0 mmol, 9.0 mL). The crude product was purified by flash chromatography (silica gel, 70:30 hexanes:EtOAc) to afford the product as a colorless oil (349.0 mg, 45% yield). Analytical data was found to be in agreement with the literature.[7]

1H NMR (400 MHz, CDCl3); δ = 5.97 (dd, J = 17.4, 10.8 Hz, 1H), 5.27 (d, J = 17.4, 1.0 Hz, 1H), 5.11 (dd, J = 10.8, 1.0 Hz, 1H), 3.88 – 3.70 (m, 4H), 1.88 – 1.77 (m, 2H), 1.57 – 1.43 (m, 3H) ppm.

1,1-Dicyclohexylprop-2-en-1-ol (A-d)
Prepared according to procedure A described above using dicyclohexylmethane K-d (1.0 equiv., 6.00 mmol, 1.16 g, 1.18 mL), THF (anhydrous, 12.0 mL) and vinyl magnesium bromide (1.0 M solution in THF, 1.3 equiv., 7.8 mmol, 7.8 mL). The crude product was purified by flash chromatography (silica gel, 90:10 hexanes:EtOAc) to afford the product as a colorless oil (1.01 g, 76% yield). Analytical data was found to be in agreement with the literature.[8]

1H NMR (300 MHz, CDCl3); δ = 5.70 (dd, J = 17.2, 11.1 Hz, 1H), 5.20-5.07 (m, 2H), 1.85 – 1.60 (m, 10H), 1.58 – 1.45 (m, 2H), 1.32 – 0.78 (m, 11H) ppm.

3-Isopropyl-4-methylpent-1-en-3-ol (A-e)
Prepared according to procedure A described above using 2,4-dimethylpentan-3-one K-e (1.0 equiv., 5.00 mmol, 570.9 mg, 708 μL), THF (anhydrous, 10.0 mL) and vinyl magnesium bromide (1.0 M solution in THF, 1.3 equiv., 6.5 mmol, 6.5 mL). The crude product was purified by flash chromatography (silica gel, 95:5 hexanes:EtOAc) to afford the product as a colorless liquid (622.0 mg, 88% yield). Analytical data was found to be in agreement with the literature.[9]

1H NMR (400 MHz, CDCl3); δ = 5.72 (dd, J = 17.2, 11.2 Hz, 1H), 5.24 – 5.14 (m, 2H), 1.91 (hept, J = 6.8 Hz, 2H), 0.88 (d, J = 6.7 Hz, 6H), 0.84 (d, J = 6.9 Hz, 6H) ppm.

2-Cyclohexylbut-3-en-2-ol (A-f)
Prepared according to procedure A described above using 1-cyclohexylethanol-1-one K-f (1.0 equiv., 6.00 mmol, 757.2 mg, 826 μL), THF (anhydrous, 12.0 mL) and vinyl magnesium bromide (1.0 M solution in THF, 1.5 equiv., 9.0 mmol, 9.0 mL). The crude product was purified by flash chromatography (silica gel, 90:10 hexanes:EtOAc) to afford the product as a colorless liquid (545 mg, 59% yield). Analytical data was found to be in agreement with the literature.[10]
\( ^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 5.91 \) (dd, \( J = 17.4, 10.8 \) Hz, 1H), 5.18 (dd, \( J = 17.4, 1.4 \) Hz, 1H), 5.06 (dd, \( J = 10.8, 1.4 \) Hz, 1H), 1.84 – 1.73 (m, 4H), 1.68 – 1.61 (m, 1H), 1.43 (br s, 1H), 1.33 (tt, \( J = 12.1, 2.9 \) Hz, 1H), 1.28 – 1.15 (m, 5H), 1.11 (tt, \( J = 12.8, 3.3 \) Hz, 1H), 1.03 – 0.92 (m, 2H) ppm.

3-Methyl-2-en-1-ol (A-g)
Prepared according to procedure A described above using octan-2-one K-g (1.0 equiv., 6.00 mmol, 769.3 mg, 939 \( \mu L \)), THF (anhysrous, 12.0 mL) and vinyl magnesium bromide (1.0 M solution in THF, 1.5 equiv., 9.0 mmol, 9.0 mL). The crude product was purified by flash chromatography (silica gel, 90:10 hexanes:EtOAc) to afford the product as a colorless liquid (784.5 mg, 84% yield). Analytical data was found to be in agreement with the literature.[11]

\( ^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta = 5.91 \) (dd, \( J = 17.4, 10.7 \) Hz, 1H), 5.19 (dd, \( J = 17.4, 1.3 \) Hz, 1H), 5.04 (dd, \( J = 10.7, 1.3 \) Hz, 1H), 1.60 – 1.40 (m, 2H), 1.40 – 1.15 (m, 12H), 0.94 – 0.81 (m, 3H) ppm.

2-Phenylbut-3-en-2-ol (A-h)
Prepared according to procedure A described above using acetophenone K-h (1.0 equiv., 6.00 mmol, 720.9 mg, 700 \( \mu L \)), THF (anhysrous, 12.0 mL) and vinyl magnesium bromide (1.0 M solution in THF, 1.3 equiv., 7.8 mmol, 7.8 mL). The crude product was purified by flash chromatography (silica gel, 90:10 hexanes:EtOAc) to afford the product as a colorless liquid (640.3 mg, 72% yield). Analytical data was found to be in agreement with the literature.[12]

\( ^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.50 – 7.45 \) (m, 2H), 7.38 – 7.31 (m, 2H), 7.29 – 7.22 (m, 1H), 6.18 (dd, \( J = 17.3, 10.6 \) Hz, 1H), 5.30 (dd, \( J = 17.3, 1.1 \) Hz, 1H), 5.15 (dd, \( J = 10.6, 1.1 \) Hz, 1H), 1.88 (br s, 1H), 1.66 (s, 3H) ppm.

4.2.2 Characterization of trifluoroacetic esters (T-a,d,e)
3-Methylbut-2-en-1-yl 2,2,2-trifluoroacetate (T-a)
Prepared according to procedure B described above using 3-methylbut-2-en-1-ol A-a (1.0 equiv., 26.00 mmol, 2.239 g, 2.64 mL), CH\(_2\)Cl\(_2\) (anhysrous, 52.0 mL), triethylamine (1.0 equiv, 26.00 mmol, 3.62 mL), 4-((dimethylamino)pyridine (0.08 equiv., 2.06 mmol, 251.6 mg) and trifluoroacetic anhydride (1.0 equiv, 26.00 mmol, 3.61 mL). The crude product was purified by flash chromatography (silica gel, 99:1 pentane:EtOAc) to afford the potentially volatile product as a colorless oil (1.377 g, 29% yield).

\( ^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 5.45 – 5.38 \) (m, 1H), 4.83 (d, \( J = 7.5 \) Hz, 2H), 1.80 (d, \( J = 1.4 \) Hz, 3H), 1.76 (d, \( J = 1.4 \) Hz, 3H) ppm. \( ^13\)C NMR (101 MHz, CDCl\(_3\)): \( \delta = 157.70 \) (q, \( J_{C,F} = 42.2 \) Hz), 142.71, 116.34, 114.72 (q, \( J_{C,F} = 285.9 \) Hz), 64.98, 25.96, 18.26 ppm. \( ^19\)F NMR (376 MHz, CDCl\(_3\)): \( \delta = -74.78 \) ppm.

3,3-Dicyclohexylallyl 2,2,2-trifluoroacetate (T-d)
Prepared according to procedure B described above using 1,1-dicyclohexylprop-2-en-1-ol A-d (1.0 equiv., 3.93 mmol, 874.3 mg), CH\(_2\)Cl\(_2\) (anhysrous, 8.0 mL), triethylamine (1.0 equiv, 3.93 mmol, 548 \( \mu L \)), 4-((dimethylamino)pyridine (0.08 equiv., 0.31 mmol, 38.0 mg) and trifluoroacetic anhydride (1.0 equiv, 3.93 mmol, 546 \( \mu L \)). The crude product was purified by flash chromatography (silica gel, pentane) to afford the product as a colorless oil (935 mg, 75% yield).
1H NMR (400 MHz, CDCl3): δ = 5.32 (t, J = 7.3 Hz, 1H), 4.92 (d, J = 7.3 Hz, 2H), 2.49 – 2.36 (m, 1H), 2.00 – 1.90 (m, 1H), 1.84 – 1.58 (m, 8H), 1.52 – 1.44 (m, 2H), 1.42 – 1.08 (m, 10H) ppm. 13C NMR (126 MHz, CDCl3): δ = 160.28, 157.70 (q, J\textsubscript{C,F} = 41.98 Hz), 114.72 (q, J\textsubscript{C,F} = 285.9 Hz), 113.90, 64.70, 41.62, 40.72, 34.70 (2C), 31.01 (2C), 27.08 (2C), 26.51 (2C), 26.30, 26.12 ppm. 19F NMR (376 MHz, CDCl3): δ = -75.24 ppm.

HRMS (ESI): m/z Calculated for [C17H25F3O2Na]+ [M+Na]+: 341.1699; found: 341.1703.

3-Isopropyl-4-methylpent-2-en-1-yl 2,2,2-trifluoroacetate (T-e)
Prepared according to procedure B described above using 3-isopropyl-4-methylpent-1-en-3-ol A-e (1.0 equiv., 4.37 mmol, 622 mg), CH\textsubscript{2}Cl\textsubscript{2} (anhydrys, 10.0 mL), triethylamine (1.0 equiv, 4.37 mmol, 609 µL), 4-(dimethylamino)pyridine (0.08 equiv., 0.35 mmol, 42 mg) and trifluoroacetic anhydride (1.0 equiv., 4.37 mmol, 608 µL). The crude product was purified by flash chromatography (silica gel, 99:1 pentane:EtOAc) to afford the product as a colorless oil (576 mg, 55% yield).

1H NMR (500 MHz, CDCl3): δ = 5.36 (t, J = 7.4 Hz, 1H), 4.92 (d, J = 7.4 Hz, 2H), 2.85 (hept, J = 6.9 Hz, 1H), 2.38 (hept, J = 6.8 Hz, 1H), 1.04 (app. dd, J = 6.9, 2.9 Hz, 12H) ppm. 13C NMR (126 MHz, CDCl3): δ = 162.02, 157.70 (q, J\textsubscript{C,F} = 41.9 Hz), 113.58 (q, J\textsubscript{C,F} = 286.02 Hz), 112.98, 64.48, 30.20, 29.02, 24.30 (2C), 21.16 (2C) ppm. 19F NMR (376 MHz, CDCl3): δ = -74.86 ppm.

4.2.3 Characterization of allyl silanes 2
Trimethyl(3-methylbut-2-en-1-yl)silane (2a)
Prepared according to the general procedure C, using trifluoroacetic ester T-a (1.0 equiv., 7.56 mmol, 1.377 g), THF (anhydrys, 30.0 mL), hexamethyldisilane (1.0 eq., 7.56 mmol, 1.55 mL) and Pd(dba)\textsubscript{2} (20 mol%, 1.51 mmol, 870 mg). The crude reaction mixture was filtered through silica gel, eluted with pentane and concentrated under reduced pressure (800 mbar, 37 °C bath). The residual oil was purified by chromatography (gravity protocol, silica gel, pentane). Combination of the clean fractions (as determined by 1H NMR) afforded the product as a volatile, colorless oil (350 mg, 32%). Analytical data was found to be in agreement with the literature.[13]

1H NMR (500 MHz, CDCl3): δ = 5.17 – 5.11 (m, 1H), 1.70 (bs, 1H), 1.56 (bs, 1H), 1.38 (d, J = 8.5, 2H), -0.02 (s, 9H) ppm.

(2-Cyclohexylideneethyl)trimethylsilane (2b)
Prepared according to general procedure D using allylic alcohol A-b (1.0 equiv., 5.11 mmol, 645.2 mg), MeOH/DMSO (anhydrys, 10.0 mL, 1:1), hexamethyldisilane (1.2 eq., 6.13 mmol, 1.26 mL) and Pd(OCOCF\textsubscript{3})\textsubscript{2} (6 mol%, 0.307 mmol, 102.0 mg). The crude product was purified by flash chromatography (silica gel, pentane) to afford the product as colorless oil (467 mg, 50%). Analytical data was found to be in agreement with the literature.[5]

1H NMR (300 MHz, CDCl3): δ = 5.09 (bt, J = 8.5, 1H), 2.11 – 2.01 (m, 4H), 1.58 – 1.43 (m, 6H), 1.39 (d, J = 8.5 Hz, 2H), -0.02 (s, 9H) ppm.

Trimethyl(2-(tetrahydro-4H-pyran-4-ylidene)ethyl)silane (2c)
Prepared according to general procedure D using allylic alcohol A-e (1.0 equiv., 2.72 mmol, 394.0 mg), MeOH/DMSO (anhydrys, 8 mL, 1:1), hexamethyldisilane (1.2 eq., 3.26 mmol, 668 µL) and Pd(OCOCF\textsubscript{3})\textsubscript{2} (5 mol%, 0.136 mmol, 45.2 mg). The crude product was purified by flash...
chromatography (silica gel, 90:10 hexanes:EtOAc) to afford the product as a colorless oil (320 mg, 64% yield). Analytical data was found to be in agreement with the literature.[14]

\[ ^{1}H \text{ NMR (300 MHz, CDCl}_3): \delta = 5.26 – 5.16 (m, 1H), 3.68 – 3.60 (m, 4H), 2.27 – 2.18 (m, 4H), 1.41 (d, J = 8.6 Hz, 2H), -0.01 (s, 9H) ppm. \]

(3,3-Dicyclohexylallyl)trimethylsilane (2d)
Prepared according to the general procedure C, using trifluoroacetic ester Td (1.0 equiv., 9.58 mmol, 3.05 g), THF (anhdyrous, 40.0 mL), hexamethyldisilane (2.0 eq., 19.16 mmol, 3.92 mL) and Pd(dba)_2 (10 mol%, 0.96 mmol, 551 mg). The crude product was purified by flash chromatography (silica gel, pentane) to afford the product as a colorless oil (1.01 g, 38% yield).

\[ ^{1}H \text{ NMR (500 MHz, CDCl}_3): \delta = 5.10 (t, J = 8.7 Hz, 1H), 2.39 – 2.30 (m, 1H), 1.83 (t, J = 11.8, 3.3 Hz, 1H), 1.78 – 1.62 (m, 6H), 1.62 – 1.51 (m, 2H), 1.46 – 1.40 (m, 4H), 1.33 – 1.24 (m, 6H), 1.20 – 1.08 (m, 4H) -0.02 (s, 9H) ppm. ^{13}C \text{ NMR (126 MHz, CDCl}_3): \delta = 147.76, 117.44, 40.21, 40.02, 35.65 (2C), 31.15 (2C), 27.51 (2C), 26.95 (2C), 26.54, 26.44, 17.94, -1.58 (3C) ppm. \]

HRMS (ESI): m/z calculated for [C_{18}H_{35}Si]^+ [M+H]^+: 279.2503, found: 279.2500.

(3-Isopropyl-4-methylpent-2-en-1-yl)trimethylsilane (2e)
Prepared according to the general procedure C, using trifluoroacetic ester T-e (1.0 equiv., 2.42 mmol, 576 mg), THF (anhdyrous, 10.0 mL), hexamethyldisilane (1 eq., 2.42 mmol, 495 µL) and Pd(dba)_2 (20 mol%, 0.48 mmol, 278.0 mg). Purified by flash chromatography (silica gel, pentane) to afford the product as a colorless oil (123.3 mg, 26%).

\[ ^{1}H \text{ NMR (400 MHz, CDCl}_3): \delta = 5.14 (t, J = 8.7 Hz, 1H), 2.78 (hept, J = 6.9 Hz, 1H), 2.28 (hept, J = 6.9 Hz, 1H), 1.44 (d, J = 8.7 Hz, 2H), 0.98 (app. dd, J = 8.1, 6.9 Hz, 12H), -0.01 (s, 9H) ppm. ^{13}C \text{ NMR (126 MHz, CDCl}_3): \delta = 148.82, 116.41, 28.81, 28.06, 25.16 (2C), 21.21 (2C), 17.86, -1.58 (3C) ppm. \]

HRMS (APCI): m/z calculated for [C_{12}H_{26}Si]^+ [M+H]^+: 198.1798, found: 198.1789.

(2-Cyclohexylprop-1-en-1-yl)trimethylsilane (2f)
Prepared according to general procedure D using allylic alcohol A-f (1.0 equiv., 3.55 mmol, 545 mg), MeOH/DMSO (anhdyrous, 10.0 mL, 1:1), hexamethyldisilane (1.2 eq., 4.24 mmol, 0.87 mL) and Pd(OCCF\_3)_2 (5 mol%, 0.177 mmol, 58.7 mg). The crude product was purified by flash chromatography (silica gel, pentane) to afford the product as a colorless oil of an inseparable mixture of E and Z isomers (525.5 mg, 71% yield, E:Z = 58:42).

\[ ^{1}H \text{ NMR (300 MHz, CDCl}_3) \text{ reported as mixture of E- and Z-:} \delta = 5.23 – 5.11 (m, 1H, E isomer), 5.10 – 5.02 (m, 1H, Z isomer), 2.38 – 2.25 (m, 1H Z isomer), 1.89 – 1.61 (m, 5H E isomer, 4H Z isomer), 1.61 – 1.58 (m, 3H, Z isomer), 1.52 (bs, 3H E isomer), 1.49 – 1.07 (m, 8H E isomer, 8H Z isomer), -0.01 (s, 9H Z isomer), -0.03 (s, 9H, E isomer) ppm. ^{13}C \text{ NMR (126 MHz, CDCl}_3) \text{ reported as mixture of E- and Z-:} \delta = 138.11, 137.82, 119.26, 118.09, 47.78, 39.36, 32.44 (2C), 31.09 (2C), 27.01 (2C), 26.92 (2C), 26.62, 26.48, 19.77, 18.46, 17.97, 14.36, -1.59 (3C), -1.60 (3C) ppm. \]

HRMS (APCI): m/z calculated for [C_{13}H_{26}Si]^+ (M^+): 210.1798, found: 210.1792.
Trimethyl(2-methyloct-1-en-1-yl)silane (2g)
Prepared according to general procedure D using allylic alcohol A-g (1.0 equiv., 5.02 mmol, 784.0 mg), MeOH/DMSO (anhydrous, 14.0 mL, 1:1), hexamethyldisilane (1.2 eq., 6.02 mmol, 1.23 mL) and Pd(OCOCF₃)₂ (5 mol%, 0.251 mmol, 83.4 mg). The crude product was purified by flash chromatography (silica gel, pentane) to afford the product as a colorless mixture of E- and Z-isomers (598.1 mg, 56% yield, E:Z = 60:40). Analytical data was found to be in agreement with the literature.[15]

(E)- or (Z)- Trimethyl(3-phenylbut-2-en-1-yl)silane (2h)
Prepared according to general procedure D using allylic alcohol A-h (1.0 equiv., 4.32 mmol, 640.3 mg), MeOH/DMSO (anhydrous, 12.0 mL, 1:1), hexamethyldisilane (1.2 eq., 5.18 mmol, 1.06 mL) and Pd(OCOCF₃)₂ (5 mol%, 0.216 mmol, 71.8 mg). Purification of the crude product by flash chromatography (silica gel, pentane) afforded the E-isomer (262.0 mg, 30% yield) and the Z-isomer as a colorless oil (163.1 mg, 19% yield), both appearing as colorless oil. Analytical data was found to be in agreement with the literature.[16]

4.3 General Procedures for the Photochemical Conjugate Addition of Allyl Groups to Enals

The procedures E & F below differ only marginally in the order of addition of reactants:

**General procedure E** (for particularly volatile prenylsilane 2a): To a dry 8 mL argon-purged glass vial equipped with a stirring bar, the amine catalyst A (20 mol%, 0.02 mmol) and the enal 1 (1.3 equiv., 0.13 mmol) was added. The vial was sealed with a septum and flushed with a stream of argon. Then, 200 µL of a pre-cooled solution of TFA (30 mol%, 0.03 mmol, 11.5 µL) in acetonitrile/1,2-dichloroethane (anhydrous, 1:1, 0.15 M) was added, followed by addition of allyl
silane 2a (1.0 equiv., 0.10 mmol) via gas-tight syringe. The vial was then irradiated as described below.

**General procedure F (for other silanes):** A dry 8 mL argon-purged glass vial equipped with a stirring bar was charged with allyl silane 2 (1 equiv, 0.1 mmol), the amine catalyst A (20 mol%, 0.02 mmol) and enal 1 (1.3 equiv., 0.13 mmol). The vial was sealed with a septum and flushed with a stream of argon. Then, 200 µL of a pre-cooled solution of TFA (30 mol%, 0.03 mmol, 11.5 µL) in acetonitrile/1,2-dichloroethane (anhydrous, 1:1, 0.15 M) was added and the vial was irradiated as described below.

**Irradiation set-up (common to procedures E and F).** The vial was then placed into an aluminum block on a 3D-printed holder, fitted with a 420 nm high-power single LED. The irradiance was fixed at 110 mW/cm², as controlled by an external power supply and measured using a photodiode light detector. This setup secured a reliable irradiation while keeping a distance of 1 cm between the reaction vessel and the light source. The temperature was kept at -15 °C with a chiller connected to the irradiation plate (the setup is detailed in Figure S5). The reaction was stirred for the indicated time (generally 22 hours), then quenched with 5 mL of NaHCO₃ and extracted three times with DCM. The combined organics were dried over MgSO₄, filtered and concentrated under vacuo. The obtained oil was then purified by flash column chromatography on silica gel to furnish the product 3.

Figure S5. Detailed set-up and illumination system. The light source for illuminating the reaction vessel consisted of a single 420 nm high-power LED.
4.3.1 Characterization of products 3

(S)-6-Methyl-3-phenyleth-5-enal (3a)

Prepared according to general procedure E using trimethyl(3-methylbut-2-en-1-yl)silane 2a (0.1 mmol, 14.2 mg), cinnamaldehyde 1a (0.13 mmol, 16.4 µL), aminocatalyst A (0.02 mmol, 14.1 mg), 100 µL of 1,2-dichloroethane and 100 µL of a 0.3 M acetonitrile solution of trifluoroacetic acid (30 mol%). Time of irradiation 22 hours. The crude mixture was purified by flash column chromatography (hexane/dichloromethane, 80:20) to afford the product as a pale yellow oil (10.2 mg, 50% yield, average of three runs, 90:10 mixture of regioisomers). The enantiomeric excess of the corresponding 2,4-dinitrophenylhydrazone (obtained upon condensation with 2,4-dinitrophenylhydrazine) was determined to be 83:17 (average of 3 runs) for the major regioisomer by UPC² analysis on a Daicel Chiralpak IE-3 column (eluent: 100% CO₂ for 1 min, gradient 100% - 60% CO₂ in CH₂CN for 5 min, 60% CO₂ in CH₃CN for 2 min, gradient 60% - 100% CO₂ in CH₃CN for 1 min; flow rate 2.0 mL/min, λ = 355 nm. Major regioisomer: τ_major = 6.39 min, τ_minor = 6.04 min.

[α]_D²⁶ = +4.1 (c = 0.3, CHCl₃, 88:12 r, 83:17 er).

¹H NMR (500 MHz, CDCl₃, major regioisomer): δ = 9.66 (t, J = 2.1 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.24 – 7.15 (m, 3H), 5.07 – 5.02 (m, 1H), 3.22 (app. p, J = 7.3 Hz, 1H), 2.83 – 2.65 (m, 2H), 2.39 – 2.25 (m, 2H), 1.65 (s, 3H), 1.54 (s, 3H), ppm. Isolated signals of the minor regioisomer: δ = 9.53 (dd, J = 2.5, 1.6 Hz, 1H), 5.82 (dd, J = 17.5, 10.8 Hz, 1H), 4.97 (dd, J = 17.5, 1.3 Hz, 1H), 3.11 (dd, J = 10.0, 5.1 Hz, 1H), 0.96 (s, 3H), 0.95 (s, 3H) ppm. ¹³C NMR (126 MHz, CDCl₃, major regioisomer): δ = 202.20, 145.05, 134.23, 128.70 ppm.

HRMS (ESI): m/z calculated for [C₁₅H₂₃O₃Na⁺] [M+CH₃OH+Na⁺]: 257.1512; found: 257.1508.

(S)-5-Cyclohexylidene-3-phenylpentanal (3b)

Prepared according to general procedure F using (2-cyclohexylideneethyl)trimethylsilane 2b (0.1 mmol, 18.2 mg), cinnamaldehyde 1a (0.13 mmol, 16.4 µL), aminocatalyst A (0.02 mmol, 14.1 mg) and 200 µL of a 0.15 M solution of trifluoroacetic acid (30 mol%) in 1,2-dichloroethane/acetonitrile 1:1. Time of irradiation 22 hours. The crude mixture was purified by flash column chromatography (hexane/dichloromethane, 80:20) to afford the product as a pale yellow (16.1 mg, 66% yield, average of three runs, 94:6 mixture of regioisomers). The enantiomeric excess of the corresponding 2,4-dinitrophenylhydrazone (obtained upon condensation with 2,4-dinitrophenylhydrazine) was determined to be 86:14 (average of 3 runs) for the major regioisomer by UPC² analysis on a Daicel Chiralpak OJ-3 column (eluent: 93% CO₂ in i-PrOH for 9 min; flow rate 2.0 mL/min, λ = 341 nm. Major regioisomer: τ_major = 6.87 min, τ_minor = 7.60 min.

[α]_D²⁶ = +3.0 (c = 0.5, CHCl₃, 93:7 r, 87:13 er).

¹H NMR (500 MHz, CDCl₃, major regioisomer): δ = 9.67 (t, J = 2.1 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.22 – 7.17 (m, 3H), 5.02 – 4.94 (m, 1H), 3.25 – 3.17 (m, 1H), 2.79 – 2.65 (m, 2H), 2.40 – 2.23 (m, 2H), 2.06 – 1.97 (m, 4H), 1.53 – 1.39 (m, 5H), 1.35 – 1.27 (m, 1H) ppm. Isolated signals of the minor regioisomer: δ = 9.52 – 9.50 (m, 1H), 5.50 (dd, J = 17.9, 11.0 Hz, 1H), 5.33 (dd, J = 11.1, 1.3 Hz, 1H), 3.08 (dd, J = 10.3, 4.9 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃, major regioisomer): δ = 202.29, 144.01, 142.28, 128.66 (2C), 127.63 (2C), 126.67, 118.27, 49.36, 40.85, 37.37, 34.56, 28.95, 28.70, 27.72, 26.95 ppm.

HRMS (ESI): m/z calculated for [C₁₇H₂₅O₃Na⁺] [M+Na⁺]: 265.1563; found: 265.1556.
(S)-3-Phenyl-5-((tetrahydro-4H-pyran-4-ylidene)pentanal (3e)
Prepared according to general procedure F using trimethyl(2-(tetrahydro-4H-pyran-4-ylidene)ethyl)silane 2c (0.1 mmol, 18.4 mg), cinnamaldehyde 1a (0.13 mmol, 16 µL), aminocatalyst A (0.02 mmol, 14.1 mg) and 200 µL of a 0.15 M solution of trifluoroacetic acid (30 mol%) in acetonitrile. Time of irradiation 22 hours. The crude mixture was purified by flash column chromatography (hexane/ethyl acetate, 90:10) to afford the product as a pale yellow oil (11.0 mg, 45% yield, single regioisomer). The enantiomeric excess of the corresponding 2,4-dinitrophenylhydrazone (obtained upon condensation with 2,4-dinitrophenylhydrazine) was determined to be 83:17 by UPC² analysis on a Daicel Chiralpak IG-3 column (eluent: 100% CO₂ for 1 min, gradient 100% - 60% CO₂ in EtOH for 5 min, 60% CO₂ in EtOH for 2 min, gradient 60% - 100% CO₂ in EtOH for 1 min; flow rate 2.0 mL/min, λ = 350 nm. τ_major = 6.53 min, τ_minor = 6.88 min. [α]D²⁶ = -3.2 (c = 0.5, CHCl₃, 100:0 rr, 83:17 er).

¹H NMR (500 MHz, CDCl₃) δ = 9.68 (t, J = 2.0 Hz, 1H), 7.32 – 7.28 (m, 2H), 7.23 – 7.20 (m, 1H), 7.19 – 7.16 (m, 2H), 5.10 (t, J = 7.6, 1H), 3.66 – 3.60 (m, 1H), 3.57 – 3.48 (m, 2H), 3.35 – 3.28 (m, 1H), 3.23 (p, J = 7.3 Hz, 1H), 2.79 – 2.71 (m, 2H), 2.42 – 2.27 (m, 2H), 2.20 – 2.04 (m, 4H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ = 201.86, 143.56, 136.82, 128.71 (2C), 127.68 (2C), 126.84, 120.17, 69.64, 68.60, 49.48, 40.55, 37.15, 34.27, 29.94 ppm. HRMS (ESI): m/z Calculated for [C₇H₃O₃Na⁺] [M+CH₃OH+Na⁺]: 299.1618; found: 299.1618.

(S)-6,6-Dicyclohexyl-3-phenylhex-5-enal (3d)
Prepared according to general procedure F using (2-cyclohexylidenecethyl)trimethylsilane 2b (0.1 mmol, 18.2 mg), cinnamaldehyde 1a (0.13 mmol, 16 µL), aminocatalyst A (0.02 mmol, 14.1 mg) and 200 µL of a 0.15 M solution of trifluoroacetic acid (30 mol%) in acetonitrile. Time of irradiation 22 hours. The crude mixture was purified by flash column chromatography (hexane/dichloromethane, 80:20) to afford the product as a pale yellow oil (17.8 mg, 53% yield, single regioisomer). The enantiomeric excess of the corresponding 2,4-dinitrophenylhydrazone (obtained upon condensation with 2,4-dinitrophenylhydrazine) was determined to be 83:17 by UPC² analysis on a Daicel Chiralpak OJ-3 column (eluent: 96% CO₂ in for 9 min; flow rate 2.0 mL/min, λ = 363 nm. τ_major = 5.09 min, τ_minor = 16.91 min. [α]D²⁶ = +3.0 (c = 0.5, CHCl₃, 93:7 rr, 83:17 er).

¹H NMR (400 MHz, CDCl₃) δ = 9.68 (t, J = 2.1 Hz, 1H), 7.32 – 7.26 (m, 2H), 7.22 – 7.15 (m, 3H), 4.99 (t, J = 7.5 Hz, 1H), 3.20 (app. p, J = 7.2 Hz, 1H), 2.82 – 2.68 (m, 2H), 2.37 (td, J = 7.3, 2.2 Hz, 2H), 2.30 – 2.21 (m, 1H), 1.79 (tt, J = 11.7, 3.2 Hz, 1H), 1.74 – 1.43 (m, 9H), 1.32 – 0.96 (m, 11H) ppm. ¹³C NMR (150 MHz, CDCl₃) δ = 202.30, 152.64, 143.97, 128.59 (2C), 127.69 (2C), 126.64, 119.09, 49.31, 41.08, 40.89, 40.21, 35.26, 35.22, 34.83, 30.96, 30.87, 27.33, 26.79, 26.75, 26.43, 26.30 ppm. HRMS (ESI): m/z calculated for [C₁₂H₁₈O₃Na⁺] [M+CH₃OH+Na⁺]: 393.2764; found: 393.2774.

(S)-6-Isopropyl-7-methyl-3-phenyloct-5-enal (3e)
Prepared according to general procedure F using (3-isopropyl-4-methylpent-2-en-1-yl)trimethylsilane 2e (0.1 mmol, 19.8 mg), cinnamaldehyde 1a (0.13 mmol, 16 µL), aminocatalyst A (0.02 mmol, 14.1 mg) and 200 µL of a 0.15 M solution of trifluoroacetic acid (30 mol%) in dichloroethane/acetonitrile 1:1. Time of irradiation 22 hours. The crude mixture was purified by flash column chromatography (hexane/ethyl acetate, 90:10) to afford the product as a pale yellow oil (7.0 mg, 40% yield, single regioisomer).
(hexane/dichloromethane, 80:20) to afford the product as a pale yellow oil (6.4 mg, 25% yield, average of three runs, single regioisomer). The enantiomeric excess of the corresponding 2,4-dinitrophenylhydrazone (obtained upon condensation with 2,4-dinitrophenylhydrazine) was determined to be 81:19 for the major regioisomer by UPC2 analysis on a Daicel Chiralpak OJ-3 column (eluent: 100% CO2 for 1 min, gradient 100% - 60% CO2 in iPrOH for 5 min, 60% CO2 in iPrOH for 2 min, gradient 60% - 100% CO2 in iPrOH for 1 min; flow rate 2.0 mL/min, λ = 344 nm. \( \tau_{\text{Major}} = 3.39 \) min, \( \tau_{\text{Minor}} = 3.57 \) min.

\([\alpha]_{D}^{26} = -4.0 \, (c = 0.2, \text{CHCl}_3, 100:0 \, \text{rr}, 81:19 \, \text{er}).\]

\( ^1\text{H NMR} \) (500 MHz, CDCl3) \( \delta = 9.68 \) (t, \( J = 2.1 \) Hz, 1H), 7.32 – 7.25 (m, 2H), 7.22 – 7.15 (m, 3H), 5.02 (t, \( J = 7.5 \) Hz, 1H), 3.21 (app. p, \( J = 7.3 \) Hz, 1H), 2.80 – 2.65 (m, 3H, 2.44 – 2.30 (m, 2H), 2.23 (app. p, \( J = 6.8 \) Hz, 1H), 0.96 – 0.89 (m, 9H), 0.83 (d, \( J = 6.9 \) Hz, 3H) ppm. \( ^{13}\text{C NMR} \) (126 MHz, CDCl3) \( \delta = 202.29, 153.82, 143.93, 128.61 \) (2C), 127.67 (2C), 126.68, 118.14, 49.37, 40.99, 34.69, 29.46, 28.32, 24.80, 24.79, 21.08, 21.02 ppm.

HRMS (ESI): m/z calculated for [C19H18O2Na]+ [M+CH3OH+Na]+: 313.2138; found: 313.2128.

(S)-6-Cyclohexyl-3-phenyleth-5-enal (3f)
Prepared according to general procedure F using an E/Z (58:42) mixture of (3-cyclohexylbut-2-en-1-yl)trimethylsilane 2f (0.1 mmol, 21.0 mg), cinnamaldehyde 1a (0.13 mmol, 16 µL), aminocatalyst A (0.02 mmol, 14.1 mg) and 200 µL of a 0.15 M solution of trifluoroacetic acid (30 mol%) in 1,2-dichloroethane/acetonitrile 1:1. Time of irradiation 22 hours. The crude mixture was purified by flash column chromatography (hexane/dichloromethane, 80:20) to afford the product as a pale yellow oil (14.9 mg, 55% yield, 95:5 mixture of regioisomers, 65:35 E/Z ratio for the major regioisomer). The enantiomeric excess of the corresponding 2,4-dinitrophenylhydrazone (obtained upon condensation with 2,4-dinitrophenylhydrazine) was determined to be 81:19 for the major regioisomer by UPC2 analysis on a Daicel Chiralpak IA-3 column (eluent: 80% CO2 in EtOH for 9 min; flow rate 2.0 mL/min, \( \lambda = 347 \) nm. Major regioisomer: \( \tau_{\text{Major}} = 7.37 \) min, \( \tau_{\text{Minor}} = 8.65 \) min.

\([\alpha]_{D}^{26} = -2.6 \, (c = 0.5, \text{CHCl}_3, 95:5 \, \text{rr}, \text{E/Z} = 65:35, 81:19 \, \text{er}).\]

\( ^1\text{H NMR} \) (500 MHz, CDCl3, major regioisomer, mixture of E/Z-isomers): \( \delta = 9.67 \) (t, \( J = 2.1 \) Hz, 1H E-isomer, 1H Z-isomer), 7.33 – 7.27 (m, 2H E-isomer, 2H Z-isomer), 7.23 – 7.17 (m, 3H E-isomer, 3H Z-isomer), 5.07 – 5.02 (m, 1H E-isomer), 4.98 – 4.93 (m, 1H, Z-isomer), 3.27 – 3.15 (m, 1H E-isomer, 1H Z-isomer), 2.82 – 2.66 (m, 2H E-isomer, 2H Z-isomer), 2.40 – 2.23 (m, 2H E-isomer, 2H Z-isomer), 1.82 – 1.56 (m, cyclohexyl of E- & Z-isomer), 1.56-1.54 (m, 3H Z-isomer), 1.48 (bs, 3H, E-isomer), 1.31 – 1.17 (m, cyclohexyl of E- & Z-isomer), 1.17 – 1.05 (m, cyclohexyl of E- & Z-isomer) ppm. Isolated signals of the minor regioisomers (= 2 diastereomers): \( \delta = 9.61 – 9.59 \) (m, 1H), 9.52 – 9.49 (m, 1H), 5.77 (dd, \( J = 17.6, 10.9 \) Hz, 1H), 5.66 (dd, \( J = 17.7, 10.9 \) Hz, 1H), 5.15 (dd, \( J = 10.9, 1.4 \) Hz, 1H), 5.14 (dd, \( J = 11.0, 1.4 \) Hz, 1H), 4.82 (dd, \( J = 17.6, 1.4 \) Hz, 1H) ppm. \( ^{13}\text{C NMR} \) (126 MHz, CDCl3, major regioisomer, mixture of E/Z-isomers): \( \delta = 202.28 \) (2C), 144.06, 143.99, 143.25, 142.80, 128.69 (2C), 128.64 (2C), 127.60 (4C), 126.69, 126.65, 120.99, 119.44, 49.51, 49.32, 47.59, 40.84, 40.69, 39.99, 35.26, 34.62, 32.02 (2C), 31.02 (2C), 26.84 (2C), 26.75, 26.72, 26.49, 26.34, 19.76, 14.66 ppm.

HRMS (ESI): m/z calculated for [C20H16O2Na]+ [M+CH3OH+Na]+: 325.2138; found: 325.2135.
(S)-6-Methyl-3-phenyldec-5-enal (3g)
Prepared according to general procedure F using an E/Z (60:40) mixture of trimethyl(3-phenylnon-2-en-1-yl)silane 2g (0.1 mmol, 21.2 mg), cinnamaldehyde 1a (0.13 mmol, 16 µL), aminocatalyst A (0.02 mmol, 14.1 mg) and 200 µL of a 0.15 M solution of trifluoroacetic acid (30 mol%) in 1,2-dichloroethane/acetonitrile 1:1. Time of irradiation 22 hours. The crude mixture was purified by flash column chromatography (hexane/dichloromethane, 80:20) to afford the product as a colorless oil (13.3 mg, 49% yield, 90:10 mixture of regioisomers, 56:44 E/Z ratio for the major regioisomer). The enantiomeric excess of the corresponding 2,4-dinitrophenyhydrazine (obtained upon condensation with 2,4-dinitrophenyhydrazine) was determined to be 80:20 for the major regioisomer by UPC² analysis on a Daicel Chiralpak OJ-3 column (eluent: 100% CO₂ for 1 min, gradient 100% - 60% CO₂ in MeCN for 5 min, 60% CO₂ in MeCN for 2 min, gradient 60% - 100% CO₂ in MeCN for 1 min; flow rate 2.0 mL/min, λ = 244 nm. Major regioisomer: τ_major = 3.31 min, τ_minor = 3.21 min.

[α]D²⁶ = -3.6 (c = 0.5, CHCl₃, 90:10 rr, E/Z = 56/44, 80:20 er).

¹H NMR (500 MHz, CDCl₃, major regioisomer, mixture of E/Z-isomers): δ = 9.68 – 9.65 (m, 1H E-isomer, 1H Z isomer), 7.34 – 7.26 (m, 2H E-isomer, 2H Z-isomer), 7.23 – 7.16 (m, 3H E-isomer, 3H Z-isomer), 5.08 – 5.00 (m, 1H E-isomer, 1H Z-isomer), 3.28 – 3.11 (m, 1H E-isomer, 1H Z-isomer), 2.84 – 2.64 (m, 2H E-isomer, 2H Z-isomer), 2.41 – 2.25 (m, 2H E-isomer, 2H Z-isomer), 1.99 – 1.88 (m, 2H E-isomer, 2H Z-isomer), 1.63 (bs, 3H Z-isomer), 1.51 (bs, 3H E-isomer), 1.35 – 1.13 (m, 8H E-isomer, 8H Z-isomer), 0.92 – 0.81 (m, 3H E-isomer, 3H Z-isomer). Isolated signals of the minor regioisomers (= 2 diastereomers): δ = 9.52 – 9.50 (m, 1H, 5.71 (dd, J = 10.9, 4.3 Hz, 1H), 5.68 (dd, J = 10.9, 4.3 Hz, 1H), 5.15 (dd, J = 10.8, 1.3 Hz, 1H), 5.09 (dd, J = 10.9, 1.3 Hz, 1H), 4.95 (dd, J = 17.6, 1.3 Hz, 1H), 4.89 (dd, J = 17.6, 1.4 Hz, 1H) ppm. ¹³C NMR (126 MHz, CDCl₃, major regioisomer, mixture of E/Z-isomers): δ = 202.24 (2C), 144.04, 144.03, 138.34, 138.19, 128.72 (2C), 128.67 (2C), 127.90 (2C), 127.57 (2C), 126.71, 126.67, 121.91, 121.27, 49.50, 49.42, 40.80, 40.68, 39.86, 35.36, 35.18, 32.07, 31.97, 31.90, 29.49, 29.04, 28.01, 27.96, 23.56, 22.56 (2C), 16.19, 16.26 (2C) ppm.

HRMS (ESI): m/z calculated for [C₁₉H₃₀O⁺] [M+Na]⁺: 295.2032; found: 295.2026.

(S,E)-3,6-Diphenylhept-5-enal (3h)
Prepared according to general procedure F using (E)-trimethyl(3-phenylbut-2-en-1-yl)silane 2h (0.1 mmol, 20.4 mg), cinnamaldehyde 1a (0.13 mmol, 16 µL), aminocatalyst A (0.02 mmol, 14.1 mg) and 200 µL of a 0.15 M solution of trifluoroacetic acid (30 mol%) in 1,2-dichloroethane/acetonitrile 1:1. Time of irradiation 22 hours. The crude mixture was purified by flash column chromatography (hexane/dichloromethane, 80:20) to afford the product as a pale yellow oil (12.6 mg, 48% yield, 64:36 mixture of regioisomers, 1:1 mixture of diastereoisomers for the minor regioisomer). The enantiomeric ratio was determined to be 71:29 for the major regioisomer by UPC² analysis on a Daicel Chiralpak IG-3 column (eluent: 100% CO₂ for 1 min, gradient 100% - 60% CO₂ in MeCN for 5 min, 60% CO₂ in MeCN for 2 min, gradient 60% - 100% CO₂ in MeCN for 1 min; flow rate 2.0 mL/min, λ = 244 nm. Major regioisomer: τ_major = 3.32 min, τ_minor = 3.10 min. This product has been prepared also with the same general procedure F, but using (Z)-trimethyl(3-phenylbut-2-en-1-yl)silane 2h as starting material. All the other reaction partners were used as stated above. The product was obtained as a pale yellow oil (12.4 mg, 47% yield, 62:38 mixture of regioisomers, 1:1 mixture of diastereoisomers for the minor regioisomer). The enantiomeric ratio was determined to be 69:31 by UPC² analysis as described above.
[a]_D^{26} = +23.4 (c = 0.5, CHCl₃, 62:38 r.r., 71:29 er).

1H NMR (500 MHz, CDCl₃, major regioisomer): δ = 9.70 (t, J = 2.0 Hz, 1H), 7.37 – 7.15 (m, 5H), 5.68 – 5.63 (m, 1H), 3.38 (app. p, J = 7.3 Hz, 1H), 2.83 – 2.80 (m, 2H), 2.71 – 2.48 (m, 2H), 1.95 (br. s, 3H) ppm. Isolated signals of the minor regioisomers (= 1:1 ratio of 2 diastereomers): δ = 9.47 (dd, J = 2.5, 1.2 Hz, 1H), 9.41 (dd, J = 2.7, 1.3 Hz, 1H), 7.11 – 7.08 (m, 2H), 7.02 – 6.97 (m, 2H), 6.40 (dd, J = 17.5, 10.9 Hz, 1H), 6.20 (dd, J = 17.5, 10.9 Hz, 1H), 5.34 (dd, J = 10.9, 1.1 Hz, 1H), 5.07 (dd, J = 10.9, 1.0 Hz, 1H), 5.01 (dd, J = 17.5, 1.1 Hz, 1H), 4.86 (dd, J = 17.4, 1.0 Hz, 1H), 3.82 (dd, J = 11.4, 3.3 Hz, 1H), 3.77 – 3.71 (m, 1H), 1.39 (s, 3H), 1.23 (s, 3H) ppm. 13C NMR (126 MHz, CDCl₃ mixture of regioisomers and diastereomers – list of signals (not assigned)): δ = 201.85, 201.79, 201.63, 143.79, 143.79, 143.79, 142.09, 139.93, 137.18, 130.20, 129.96, 128.80, 128.47, 128.31, 128.25, 127.81, 127.62, 127.60, 127.01, 126.97, 126.92, 126.87, 126.80, 126.60, 126.44, 125.81, 125.23, 116.08, 113.87, 49.57, 49.48, 49.25, 45.47, 45.19, 40.45, 36.05, 23.75, 21.72, 16.17 ppm.

HRMS (ESI): m/z calculated for [C₂₀H₂₅O₃Na]⁺ [M+CH₃OH+Na]⁺: 319.1669; found: 319.1670.

(S)-5-Cyclohexylidene-3-(4-nitrophenyl)pentanal (3i)
Prepared according to general procedure F using (2-cyclohexylidenecarbethoxy)trimethylsilane 2b (0.1 mmol, 18.2 mg), 3-(4-nitrophenyl)acrylaldehyde 1c (0.13 mmol, 23 mg), aminocatalyst A (0.02 mmol, 14.1 mg) and 200 µL of a 0.15 M solution of trifluoroacetic acid (30 mol%) in 1,2-dichloroethane/acetonitrile 1:1. Time of irradiation 22 hours. The crude mixture was purified by flash column chromatography (hexane/dichloromethane, 60:40) to afford the product as a yellow oil (15.8 mg, 55% yield, 98:2 mixture of regioisomers). The enantiomeric excess of the corresponding 2,4-dinitrophenylhydrazone (obtained upon condensation with 2,4-dinitrophenylhydrazine) was determined to be 88:12 for the major regioisomer by UPC² analysis on a Daicel Chiralpak IG-3 column (eluent: 100% CO₂ for 1 min, gradient 100% - 60% CO₂ in EtOH for 5 min, 60% CO₂ in EtOH for 2 min, gradient 60% - 100% CO₂ in EtOH for 1 min; flow rate 2.0 mL/min, λ = 349 nm. Major regioisomer: τ_major = 7.25 min, τ_minor = 7.84 min.

[a]_D^{26} = -4.9 (c = 0.5, CHCl₃, 98:2 r.r., 88:12 er).

1H NMR (500 MHz, CDCl₃, major regioisomer) δ = 9.69 (t, J = 1.5 Hz, 1H), 8.17 – 8.13 (m, 2H), 7.37 – 7.34 (m, 2H), 4.92 (br. t, J = 7.9 Hz, 1H), 3.35 (app. p, J = 7.3 Hz, 1H), 2.86 (ddd, J = 17.4, 6.1, 1.5 Hz, 1H) 2.77 (ddd, J = 17.4, 8.2, 1.7 Hz, 1H), 2.42 – 2.26 (m, 2H), 2.06 – 1.94 (m, 4H), 1.53 – 1.36 (m, 5H), 1.35 – 1.20 (m, 1H) ppm. Isolated signals of the minor regioisomer: δ = 9.58 (br. dd, J = 2.1, 1.1 Hz, 1H), 5.47 (dd, J = 17.7, 11.0 Hz, 1H), 5.38 (dd, J = 11.0, 1.4 Hz, 1H), 3.25 (dd, J = 10.4, 4.1 Hz, 1H), 13C NMR (126 MHz, CDCl₃, major regioisomer) δ = 200.53, 151.93, 146.80, 143.19, 128.59 (2C), 123.87 (2C), 117.20, 49.07, 40.36, 37.31, 34.03, 28.93, 28.67, 27.76, 26.81 ppm.

HRMS (ESI): m/z calculated for [C₁₈H₂₅NO₄Na]⁺ [M+CH₃OH+Na]⁺: 342.1676; found: 342.1679.

(S)-5-Cyclohexylidene-3-(4-(trifluoromethyl)phenyl)pentanal (3j)
Prepared according to general procedure F using (2-cyclohexylidenecarbethoxy)trimethylsilane 2b (0.1 mmol, 18.2 mg), 3-(4-(trifluoromethyl)phenyl)acrylaldehyde 1b (0.13 mmol, 26 mg), aminocatalyst A (0.02 mmol, 14.1 mg) and 200 µL of a 0.15 M solution of trifluoroacetic acid (30 mol%) in 1,2-dichloroethane/acetonitrile 1:1. Time of irradiation 48 hours. The crude mixture was purified by flash column chromatography (hexane/dichloromethane, 80:20) to afford the product as a pale yellow oil (13.3 mg, 43% yield, 99:1 mixture of regioisomers). The enantiomeric excess of the corresponding 2,4-dinitrophenylhydrazone...
(obtained upon condensation with 2,4-dinitrophenyldiazine) was determined to be 88:12 for the major regioisomer by UPC² analysis on a Daicel Chiralpak IG-3 column (eluent: 100% CO₂ for 1 min, gradient 100% - 60% CO₂ in EtOH for 5 min, 60% CO₂ in EtOH for 2 min, gradient 60% - 100% CO₂ in EtOH for 1 min; flow rate 2.0 mL/min, λ = 347 nm. Major regioisomer: τ_major = 4.62 min, τ_minor = 4.95 min.

[α]D²⁶ = -1.0 (c = 0.5, CHCl₃; 99:1 rr, 88:12 er).

¹H NMR (500 MHz, CDCl₃, major regioisomer): δ = 9.68 (t, J = 1.8 Hz, 1H), 7.55 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 4.95 (t, J = 7.5 Hz, 1H), 3.29 (app. p, J = 13.7, 1H), 2.82 (ddd, J = 17.1, 6.3, 1.7 Hz, 1H), 2.74 (ddd, J = 17.1, 8.2, 1.9 Hz, 1H), 2.40-2.24 (m, 2H), 2.01 (m, 4H), 1.53 – 1.35 (m, 5H), 1.33-1.23 (m, 1H) ppm. ¹³C NMR (101 MHz, CDCl₃, major regioisomer): δ = 201.20, 148.20, 142.84, 129.00 (q, J_F-C,F = 32.3 Hz), 128.05 (2C), 125.58 (q, J_F-C,F = 3.8 Hz, 2C), 124.34 (q, J_F-C,F = 271.9 Hz), 117.63, 49.16, 40.46, 37.35, 34.24, 28.94, 28.69, 27.72, 26.87 ppm. ¹⁹F NMR (376 MHz, CDCl₃, major regioisomer): δ = -62.5 ppm.

HRMS (ESI): m/z calculated for [C₁₀H₂₅F₂NaO₂]⁺ [M+CH₃OH+Na⁺]: 365.1699; found: 365.1686.

(S)-5-Cyclohexylidene-3-(4-fluorophenyl)pentanal (3k)
Prepared according to general procedure F using (2-cyclohexylideneethyl)trimethylsilane 2b (0.1 mmol, 18.2 mg), (E)-3-(4-fluorophenyl)acrylaldehyde 1d (0.13 mmol, 19.5 mg), aminocatalyst A (0.02 mmol, 14.1 mg) and 200 µL of a 0.15 M solution of trifluoroacetic acid (30 mol%) in 1,2-dichloroethane/acetonitrile 1:1. Time of irradiation 22 hours. The crude mixture was purified by flash column chromatography (hexane/dichloromethane, 80:20) to afford the product as a pale yellow oil (14.3 mg, 55% yield, 94:6 mixture of regioisomers). The enantiomeric excess of the corresponding 2,4-dinitrophenyldiazine (obtained upon condensation with 2,4-dinitrophenyldiazine) was determined to be 80:20 for the major regioisomer by UPC² analysis on a Daicel Chiralpak OJ-3 column (eluent: 100% CO₂ for 1 min, gradient 100% - 60% CO₂ in MeOH for 5 min, 60% CO₂ in MeOH for 2 min, gradient 60% - 100% CO₂ in MeOH for 1 min; flow rate 2.0 mL/min, λ = 348 nm. Major regioisomer: τ_major = 4.34 min, τ_minor = 4.58 min.

[α]D²⁶ = -1.0 (c = 0.5, CHCl₃; 94:6 rr, 80:20 er).

¹H NMR (500 MHz, CDCl₃, major regioisomer): δ = 9.66 (t, J = 2.0 Hz, 1H), 7.17 – 7.11 (m, 2H), 7.01 – 6.95 (m, 2H), 4.95 (br. t, J = 7.9 Hz, 1H), 3.25 – 3.16 (m, 1H), 2.76 (ddd, J = 16.7, 6.3, 1.9 Hz, 1H), 2.67 (ddd, J = 16.7, 8.3, 2.1 Hz, 1H), 2.38 – 2.19 (m, 2H), 2.06 – 1.94 (m, 4H), 1.54 – 1.38 (m, 5H), 1.36 – 1.23 (m, 1H) ppm. Isolated signals of the minor regioisomer: δ = 9.52 (br. dd, J = 2.8, 1.5 Hz, 1H), 5.47 (dd, J = 17.8, 11.0 Hz, 1H), 5.34 (dd, J = 11.1, 1.4 Hz, 1H), 3.08 (dd, J = 10.8, 4.3 Hz, 1H) ppm. ¹³C NMR (126 MHz, CDCl₃, major regioisomer): δ = 201.86, 161.63 (d, J_C-F = 244.46 Hz), 142.45, 139.65 (d, J_C-F = 3.21 Hz), 129.03 (d, J_C-F = 7.84 Hz, 2C), 118.00, 115.40 (d, J_C-F = 21.14, 2C), 49.52, 40.02, 37.35, 34.59, 28.93, 28.70, 27.73, 26.91 ppm. ¹⁹F NMR (376 MHz, CDCl₃, major regioisomer): δ = -116.7 ppm.

HRMS (ESI): m/z calculated for [C₁₈H₂₅FO₂Na⁺] [M+CH₃OH+Na⁺]: 315.1731; found: 315.1735.
(S)-3-(4-Chlorophenyl)-5-cyclohexylidenepentanal (3l)
Prepared according to general procedure F using (2-cyclohexylideneneethyl)trimethylsilane 2b (0.1 mmol, 18.2 mg), 3-(4-chlorophenyl)acrylaldehyde 1e (0.13 mmol, 21.7 mg), aminocatalyst A (0.02 mmol, 14.1 mg) and 200 µL of a 0.15 M solution of trifluoroacetic acid (30 mol%) in 1,2-dichloroethane/acetonitrile 1:1. Time of irradiation 22 hours. The crude mixture was purified by flash column chromatography (hexane/dichloromethane, 80:20) to afford the product as a yellow oil (14.7 mg, 53% yield, 95:5 mixture of regioisomers). The enantiomeric excess of the corresponding 2,4-dinitrophenylhydrazone (obtained upon condensation with 2,4-dinitrophenylhydrazine) was determined to be 85:15 for the major regioisomer by UPC² analysis on a Daicel Chiralpak IG-3 column (eluent: 100% CO₂ for 1 min, gradient 100% - 60% CO₂ in EtOH for 5 min, 60% CO₂ in EtOH for 2 min, gradient 60% - 100% CO₂ in EtOH for 1 min; flow rate 2.0 mL/min, λ = 349 nm. Major regioisomer: τₘajo = 8.14 min, τₘino = 8.64 min.

[α]D² = -1.3 (c = 0.5, CHCl₃, 95:5 rr, 85:15 er).

¹H NMR (500 MHz, CDCl₃, major regioisomer): δ = 9.67 (t, J = 1.9 Hz, 1H), 7.29 – 7.25 (m, 2H), 7.15 – 7.11 (m, 2H), 4.95 (br. t, J = 8.0 Hz, 1H), 3.27 – 3.14 (m, 1H), 2.77 (ddd, J = 16.9, 6.3, 1.9 Hz, 1H), 2.80 (ddd, J = 16.9, 8.3, 2.0 Hz, 1H), 2.38 – 2.21 (m, 2H), 2.08 – 1.97 (m, 4H), 1.54 – 1.39 (m, 5H), 1.38 – 1.30 (m, 1H) ppm. Isolated signals of the minor regioisomer: δ = 9.53 (br. dd, J = 2.6, 1.4 Hz, 1H), 5.47 (dd, J = 17.8, 11.1 Hz, 1H), 5.35 (dd, J = 11.0, 1.4 Hz, 1H), 3.08 (br. dd, J = 10.7, 4.3 Hz, 1H) ppm. ¹³C NMR (126 MHz, CDCl₃, major regioisomer): δ = 201.64, 142.58, 142.51, 132.31, 129.01 (2C), 128.75 (2C), 117.86, 49.34, 40.12, 37.35, 34.37, 28.94, 28.69, 27.74, 26.90 ppm.

HRMS (ESI): m/z calculated for [C₈H₅ClO₂Na]⁺ [M+CH₃OH+Na]⁺: 331.1435; found: 331.1437.

(S)-3-(4-Bromophenyl)-5-cyclohexylidenepentanal (3m)
Prepared according to general procedure F using (2-cyclohexylideneneethyl)trimethylsilane 2b (0.1 mmol, 18.2 mg), (E)-3-(4-bromophenyl)acrylaldehyde 1f (0.13 mmol, 27.4 mg), aminocatalyst A (0.02 mmol, 14.1 mg) and 200 µL of a 0.15 M solution of trifluoroacetic acid (30 mol%) in 1,2-dichloroethane/acetonitrile 1:1. Time of irradiation 22 hours. The crude mixture was purified by flash column chromatography (hexane/dichloromethane, 80:20) to afford the product as a yellow oil (16.9 mg, 53% yield, 93:7 mixture of regioisomers). The enantiomeric excess of the corresponding 2,4-dinitrophenylhydrazone (obtained upon condensation with 2,4-dinitrophenylhydrazine) was determined to be 83:17 for the major regioisomer by UPC² analysis on a Daicel Chiralpak ID-3 column (eluent: 100% CO₂ for 1 min, gradient 100% - 70% CO₂ in iPrOH for 5 min, 70% CO₂ in iPrOH for 2 min, gradient 70% - 100% CO₂ in iPrOH for 1 min; flow rate 2.0 mL/min, λ = 346 nm. Major regioisomer: τₘajo = 8.34 min, τₘino = 8.14 min.

[α]D² = -0.7 (c = 0.5, CHCl₃, 93:7 rr, 83:17 er).

¹H NMR (500 MHz, CDCl₃, major regioisomer) δ = 9.66 (t, J = 1.9 Hz, 1H), 7.44 – 7.39 (m, 2H), 7.09 – 7.05 (m, 2H), 4.94 (br. t, J = 7.9 Hz, 1H), 3.23 – 3.13 (m, 1H), 2.76 (ddd, J = 16.9, 6.3, 1.9 Hz, 1H), 2.67 (ddd, J = 16.9, 8.3, 1.9 Hz, 1H), 2.37 – 2.21 (m, 2H), 2.05 – 1.97 (m, 4H), 1.54 – 1.38 (m, 5H), 1.38 – 1.29 (m, 1H). Isolated signals of the minor regioisomer: δ = 9.52 (br. dd, J = 2.7, 1.4 Hz, 1H), 5.46 (dd, J = 17.9, 11.0 Hz, 1H) 5.34 (dd, J = 11.0, 1.3 Hz, 1H) ppm. ¹³C NMR (126 MHz, CDCl₃, major regioisomer) δ = 201.58, 143.05, 142.61, 131.70 (2C), 129.41 (2C), 120.36, 117.84, 49.28, 40.17, 37.34, 34.31, 28.94, 28.70, 27.74, 26.91 ppm.
HRMS (ESI): m/z calculated for [C\textsubscript{17}H\textsubscript{23}BrNaO]\textsuperscript{+} [M+Na]\textsuperscript{+}: 343.0668; found: 343.0667.

(S)-5-Cyclohexylidene-3-(p-toly)pentanal (3n)
Prepared according to general procedure F using (2-cyclohexylideneneethyl)trimethylsilane 2b (0.1 mmol, 18.2 mg), (E)-3-(p-toly)acyraldehyde 1g (0.13 mmol, 19.0 mg), aminocatalyst A (0.02 mmol, 14.1 mg) and 200 µL of a 0.15 M solution of trifluoroacetic acid (30 mol%) in 1,2-dichloroethane/acetoneitrile 1:1. Time of irradiation 22 hours. The crude mixture was purified by flash column chromatography (hexane/dichloromethane, 80:20) to afford the product as a pale yellow oil (9.9 mg, 39% yield, 86:14 mixture of regioisomers). The enantiomeric excess of the corresponding 2,4-dinitrophenylhydrazone (obtained upon condensation with 2,4-dinitrophenylhydrazine) was determined to be 75:25 for the major regioisomer by UPC\textsuperscript{2} analysis on a Daicel Chiralpak OJ-3 column (eluuent: 100% CO\textsubscript{2} for 1 min, gradient 100% - 80% CO\textsubscript{2} in EtOH for 5 min, 80% CO\textsubscript{2} in EtOH for 2 min, gradient 80% - 100% CO\textsubscript{2} in EtOH for 1 min; flow rate 2.0 mL/min, λ = 349 nm. Major regioisomer: τ\textsubscript{Major} = 5.46 min, τ\textsubscript{Minor} = 5.09 min.

[α]\textsubscript{D}\textsuperscript{26} = +1.1 (c = 0.4, CHCl\textsubscript{3}, 86:14 τ, 75:25 er).

\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, major regioisomer) δ = 9.65 (t, J = 2.2 Hz, 1H), 7.12 – 6.99 (m, 4H), 5.01 – 4.96 (m, 1H), 3.21 – 3.12 (m, 1H), 2.73 – 2.70 (m, 1H), 2.66 (ddd, J = 16.5, 8.4, 2.3 Hz, 1H), 2.38 – 2.23 (m, 5H), 2.10 – 1.98 (m, 4H), 1.54 – 1.40 (m, 5H), 1.41 – 1.31 (m, 1H).

Isolated signals of the minor regioisomer: δ = 9.50 (br. dd, J = 2.8, 1.7 Hz, 1H), 5.50 (dd, J = 17.9, 11.0 Hz, 1H), 5.32 (dd, J = 11.0, 1.4 Hz, 1H) ppm. \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}, major regioisomer) δ = 202.50, 142.18, 140.98, 136.17, 129.35 (2C), 127.45 (2C), 118.41, 49.43, 40.49, 37.36, 34.62, 28.97, 28.71, 27.74, 26.97, 21.14 ppm.

HRMS (ESI): m/z calculated for [C\textsubscript{19}H\textsubscript{20}O\textsubscript{2}Na]\textsuperscript{+} [M+CH\textsubscript{3}OH+Na]\textsuperscript{+}: 311.1982; found: 311.1972.

(S)-5-Cyclohexylidene-3-(m-toly)pentanal (3o)
Prepared according to general procedure F using (2-cyclohexylideneneethyl)trimethylsilane 2h (0.1 mmol, 18.2 mg), (E)-3-(m-toly)acyraldehyde 1h (0.13 mmol, 19.0 mg), aminocatalyst A (0.02 mmol, 14.1 mg) and 200 µL of a 0.15 M solution of trifluoroacetic acid (30 mol%) in 1,2-dichloroethane/acetoneitrile 1:1. Time of irradiation 22 hours. The crude mixture was purified by flash column chromatography (hexane/dichloromethane, 80:20) to afford the product as a pale yellow oil (12.8 mg, 50% yield, 91:9 mixture of regioisomers). The enantiomeric excess of the corresponding 2,4-dinitrophenylhydrazone (obtained upon condensation with 2,4-dinitrophenylhydrazine) was determined to be 79:21 for the major regioisomer by UPC\textsuperscript{2} analysis on a Daicel Chiralpak OJ-3 column (eluuent: 100% CO\textsubscript{2} for 1 min, gradient 100% - 90% CO\textsubscript{2} in EtOH for 5 min, 90% CO\textsubscript{2} in EtOH for 2 min, gradient 90% - 100% CO\textsubscript{2} in EtOH for 1 min; flow rate 2.0 mL/min, λ = 349 nm. Major regioisomer: τ\textsubscript{Major} = 7.40 min, τ\textsubscript{Minor} = 7.14 min.

[α]\textsubscript{D}\textsuperscript{26} = +1.9 (c = 0.5, CHCl\textsubscript{3}, 91:9 τ, 79:21 er).

\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, major regioisomer) δ = 9.66 (t, J = 2.2 Hz, 1H), 7.18 (br. t, J = 7.3, 1H), 7.04 – 6.96 (m, 3H), 5.03 – 4.97 (m, 1H), 3.17 (app. p, J = 7.3 Hz, 1H), 2.74 (ddd, J = 16.6, 6.5, 2.2 Hz, 1H), 2.68 (ddd, J = 16.6, 8.3, 2.2 Hz, 1H), 2.41 – 2.20 (m, 5H), 2.10 – 1.97 (m, 4H), 1.55 – 1.37 (m, 5H), 1.38 – 1.20 (m, 1H) ppm. Isolated signals of the minor regioisomer: δ = 9.50 (dd, J = 2.6, 1.8 Hz, 1H), 5.51 (dd, J = 17.9, 11.1 Hz, 1H), 5.33 (dd, J = 11.1, 1.4 Hz, 1H), 3.03 (dd, J = 10.3, 5.0 Hz, 1H) ppm. \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}, major regioisomer) δ = 202.47, 143.98, 142.20, 138.19, 128.54, 128.39, 127.42, 124.60, 118.40, 49.34, 40.83, 37.37, 34.59, 28.97, 28.72, 27.71, 26.96, 21.63 ppm.

HRMS (ESI): m/z calculated for [C\textsubscript{19}H\textsubscript{20}O\textsubscript{2}Na]\textsuperscript{+} [M+CH\textsubscript{3}OH+Na]\textsuperscript{+}: 311.1982; found: 311.1971.
(S)-5-Cyclohexylidene-3-(o-tolyl)pentanal (3p)
Prepared according to general procedure F using (2-cyclohexylideneethytrimethylsilane 2b (0.1 mmol, 18.2 mg), (E)-3-(o-tolyl)acrylaldehyde 1i (0.13 mmol, 19.0 mg), aminocatalyst A (0.02 mmol, 14.1 mg) and 200 µL of a 0.15 M solution of trifluoroacetic acid (30 mol%) in 1,2-dichloroethane/acetoniitrile 1:1. Time of irradiation 22 hours. The crude mixture was purified by flash column chromatography (hexane/dichloromethane, 80:20) to afford the product as a pale yellow oil (12.8 mg, 50% yield, 90:10 mixture of regioisomers). The enantiomeric excess of the corresponding 2,4-dinitrophenylhydrazone (obtained upon condensation with 2,4-dinitrophenylhydrazine) was determined to be 80:20 for the major regioisomer by UPC^2 analysis on a Daicel Chiralpak ID-3 column (elucent: 85% CO in MeCH for 9 min; flow rate 2.0 mL/min, λ = 394 nm. Major regioisomer: τ_major = 6.83 min, τ_minor = 6.39 min.

[α]_D^26 = +6.1 (c = 0.5, CHCl₃, 90:10 τr, 80:20 er).

^1H NMR (500 MHz, CDCl₃, major regioisomer) δ = 9.65 (t, J = 2.0 Hz, 1H), 7.20 – 7.12 (m, 3H), 7.11 – 7.07 (m, 1H), 5.04 – 4.97 (m, 1H), 3.50 (app. p, J = 7.2 Hz, 1H), 2.81 – 2.65 (m, 2H), 2.37 (s, 3H), 2.35 – 2.21 (m, 2H), 2.09 – 1.96 (m, 4H), 1.53 – 1.37 (m, 5H), 1.35 – 1.23 (m, 1H) ppm. Isolated signals of the minor regioisomer: δ = 9.48 (br. dd, J = 2.4, 1.6 Hz, 1H), 5.58 (dd, J = 18.0, 11.1 Hz, 1H), 5.37 (dd, J = 11.1, 1.3 Hz, 1H), 3.41 (dd, J = 10.6, 4.5 Hz, 1H), 2.43 (s, 3H), ppm. ^13C NMR (126 MHz, CDCl₃, major regioisomer) δ: 202.24, 142.27, 142.20, 135.87, 130.58, 126.41, 126.28, 126.04, 118.27, 49.33, 37.38, 35.53, 34.19, 34.19, 28.90, 28.66, 27.71, 26.95, 19.95 ppm.

HRMS (ESI): m/z calculated for [C_19H_20O_2Na]^+ [M+CH_3OHNa]^+: 311.1982; found: 311.1977.

(S)-5-Cyclohexylidene-3-(3-methoxyphenyl)pentanal (3q)
Prepared according to general procedure F using (2-cyclohexylideneethytrimethylsilane 2b (0.1 mmol, 18.2 mg), 3-(3-methoxyphenyl)acrylaldehyde 1j (0.13 mmol, 23 mg), aminocatalyst A (0.02 mmol, 14.1 mg) and 200 µL of a 0.15 M solution of trifluoroacetic acid (30 mol%) in 1,2-dichloroethane/acetoniitrile 1:1. Time of irradiation 48 hours. The crude mixture was purified by flash column chromatography (hexane/dichloromethane, 50:50) to afford the product as a yellow oil (15.2 mg, 56% yield, 90:10 mixture of regioisomers). The enantiomeric excess of the corresponding 2,4-dinitrophenylhydrazone (obtained upon condensation with 2,4-dinitrophenylhydrazine) was determined to be 80:20 for the major regioisomer by UPC^2 analysis on a Daicel Chiralpak IG-3 column (elucent: 100% CO in MeCH for 1 min, gradient 100% - 60% CO_2 in EtOH for 5 min, 60% CO_2 in EtOH for 2 min, gradient 60% - 100% CO_2 in EtOH for 1 min; flow rate 2.0 mL/min, λ = 349 nm. Major regioisomer: τ_major = 5.38 min, τ_minor = 5.20 min.

[α]_D^26 = +2.0 (c = 0.5, CHCl₃, 90:10 τr, 80:20 er).

^1H NMR (400 MHz, CDCl₃, major regioisomer): δ = 9.66 (t, J = 2.1 Hz, 1H), 7.25 – 7.12 (m, 1H), 6.82 – 6.69 (m, 3H), 5.02 – 4.96 (m, 1H), 3.80 (s, 3H), 3.23 – 3.13 (m, 1H), 2.80 – 2.61 (m, 2H), 2.38-2.24 (m, 2H), 2.08 – 1.98 (m, 4H), 1.54 – 1.38 (m, 5H), 1.39 – 1.23 (m, 1H) ppm. Isolated signals of the minor regioisomer: δ = 9.51 (br. dd, J = 2.6, 1.8 Hz, 1H), 5.52 (dd, J = 17.8, 11.0 Hz, 1H), 5.34 (dd, J = 11.0, 1.4 Hz, 1H), 3.05 (dd, J = 10.2, 5.0 Hz, 1H) ppm. ^13C NMR (101 MHz, CDCl₃, major regioisomer): δ: 202.22, 159.85, 145.73, 142.29, 129.64, 119.98, 118.27, 113.71, 111.68, 111.64, 55.32, 49.30, 40.91, 37.37, 34.47, 28.97, 28.71, 27.74, 26.95 ppm.
HRMS (ESI): m/z calculated for [C_{19}H_{23}O_{3}Na]^+ [M+CH_{3}OH+Na]^+: 327.1931; measured: 327.1925

(S)-5-Cyclohexylidene-3-(4 (trimethylsilyl)phenyl)pentanal (3r)
Prepared according to general procedure F using (2-cyclohexylidencyclohexyl)trimethylsilane 2b (0.1 mmol, 18.2 mg), 3-(4-(trimethylsilyl)phenyl)acrylaldehyde 1k (0.13 mmol, 26.6 mg), aminocatalyst A (0.02 mmol, 14.1 mg) and 200 µL of a 0.15 M solution of trifluoroacetic acid (30 mol%) in 1,2-dichloroethane/acetonitrile 1:1. Time of irradiation 22 hours. The crude mixture was purified by flash column chromatography (hexane/dichloromethane, 80:20) to afford the product as a white waxy solid (20.8 mg, 66% yield, 95:5 mixture of regioisomers). The enantiomeric ratio was determined to be 80:20 for the major regioisomer by UPC² analysis on a Daicel Chiralpak IG-3 column (eluent: 100% CO₂ for 1 min, gradient 100% - 60% CO₂ in MeOH for 5 min, 60% CO₂ in MeOH for 2 min, gradient 60% - 100% CO₂ in MeOH for 1 min; flow rate 2.0 mL/min, λ = 354 nm). Major regioisomer: [α]_D = +1.2 (c = 0.3, CHCl₃). Minor regioisomer: [α]_D = -0.7 (c = 1.0, CHCl₃).

1H NMR (400 MHz, CDCl₃, major regioisomer) δ = 9.67 (t, J = 2.1 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.18 (d, J = 7.9 Hz, 1H), 5.00 (br. t, J = 7.5 Hz, 1H), 3.20 (app. p, J = 7.2 Hz, 1H), 2.80 – 2.65 (m, 2H), 2.40-2.23 (m, 2H), 2.09 – 1.98 (m, 4H), 1.54 – 1.35 (m, 5H), 1.33 – 1.18 (m, 1H), 0.25 (s, 9H) ppm. Isolated signals of the minor regioisomer: δ = 9.51 (br. dd, J = 2.6, 1.8 Hz, 1H), 5.51 (dd, J = 17.8, 11.0 Hz, 1H), 5.33 (dd, J = 11.1, 1.4 Hz, 1H), 3.07 (dd, J = 10.0, 5.1 Hz, 1H) ppm. 13C NMR (126 MHz, CDCl₃, major regioisomer) δ = 202.33, 144.59, 142.29, 138.50, 133.70 (2C), 127.06 (2C), 118.31, 49.16, 40.77, 37.39, 34.54, 28.95, 28.68, 27.66, 26.94, -0.96 ppm.

HRMS (ESI): m/z calculated for [C_{21}H_{33}NaO_{3}Si]^+ [M+CH_{3}OH+Na]^+: 369.2220; found: 369.2203.

(S)-6-Methyl-3-(4-(trifluoromethyl)phenyl)hept-5-enal (3s)
Prepared according to general procedure E using trimethyl(3-methylbut-2-en-1-yl)silane 2a (0.1 mmol, 19.0 µL), 3-(4-(trifluoromethyl)phenyl)acrylaldehyde 1b (0.13 mmol, 26.0 mg), aminocatalyst A (0.02 mmol, 14.1 mg) and 200 µL of a 0.15 M solution of trifluoroacetic acid (30 mol%) in 1,2-dichloroethane/acetonitrile 1:1. Time of irradiation 96 hours. The crude mixture was purified by flash column chromatography (hexane/dichloromethane, 80:20) to afford the product as a white waxy solid (12.0 mg, 44% yield, 94:6 mixture of regioisomers). The enantiomeric excess of the corresponding 2,4-dinitrophenyldiazride (obtained upon condensation with 2,4-dinitrophenyldiazine) was determined to be 84:16 for the major regioisomer by UPC² analysis on a Daicel Chiralpak IG-3 column (eluent: 100% CO₂ for 1 min, gradient 100% - 70% CO₂ in MeOH for 5 min, 70% CO₂ in MeOH for 2 min, gradient 70% - 100% CO₂ in MeOH for 1 min; flow rate 2.0 mL/min, λ = 346 nm). Major regioisomer: [α]_D = +0.72 (c = 0.3, CHCl₃). Minor regioisomer: [α]_D = +1.2 (c = 0.3, CHCl₃).

1H NMR (500 MHz, CDCl₃, major regioisomer): δ = 9.67 (t, J = 1.8 Hz, 1H), 7.55 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 5.03 – 4.97 (m, 1H), 3.30 (app. p, J = 7.3 Hz, 1H), 2.80 (ddd, J = 17.1, 6.3, 1.8 Hz, 1H), 2.73 (ddd, J = 17.1, 8.2, 1.9 Hz, 1H), 2.41 – 2.24 (m, 2H), 1.65 (br. s, 3H), 1.53 (br. s, 3H) ppm. Isolated signals of the minor regioisomer: δ = 9.56 (t, J = 1.8 Hz, 1H).
5.79 (dd, J = 17.4, 10.8 Hz, 1H), 5.08 (dd, J = 10.7, 1.1 Hz, 1H), 3.22–3.18 (m, 1H), 0.97 (s, 1H), 0.94 (s, 1H) ppm. 13C NMR (126 MHz, CDCl3): δ = 201.17, 148.22, 134.80, 129.01 (q, J = 32.4 Hz), 127.96 (2C), 125.63 (q, J = 3.8 Hz, 2C), 124.34 (q, J = 272.1 Hz), 121.00, 49.23, 40.28, 35.12, 25.87, 17.99 ppm. 19F NMR (376 MHz, CDCl3, major regioisomer): -62.5 ppm.

HRMS (APCI): m/z calculated for [C15H18F3O]+ [M+H]+: 371.1304; found: 371.1303.

(S)-6-Methyl-3-(4-nitrophenyl)hept-5-enal (3I)
Prepared according to general procedure E using trimethyl(3-methylbut-2-en-1-yl)silane 2a (0.1 mmol, 19.0 μL), 3-(4-nitrophenyl)acrylaldehyde 1c (0.13 mmol, 23.0 mg), aminocatalyst A (0.02 mmol, 14.1 mg) and 200 μL of a 0.15 M solution of trifluoroacetic acid (30 mol%) in 1,2-dichloroethane/acetonitrile 1:1. Time of irradiation 62 hours. The crude mixture was purified by flash column chromatography (hexane/dichloromethane, 60:40) to afford the product as a white waxy solid (8.7 mg, 35% yield, 94:6 mixture of regioisomers). The enantiomeric excess of the corresponding 2,4-dinitrophenylhydrazone (obtained upon condensation with 2,4-dinitrophenylhydrazine) was determined to be 87:13 for the major regioisomer by UPC analysis on a Daicel Chiralpak ID-3 column (eluent: 100% CO2 for 1 min, gradient 100% - 70% CO2 in MeOH for 11 min, 70% CO2 in MeOH for 2 min, gradient 70% - 100% CO2 in MeOH for 1 min; flow rate 2.0 mL/min, λ = 346 nm. Major regioisomer: τMajor = 13.78 min, τMinor = 13.55 min.

[α]D h = -3.7 (c = 0.2, CHCl3, 94:6 rr, 87:13 er).

1H NMR (500 MHz, CDCl3, major regioisomer): δ = 9.69 (t, J = 1.5 Hz, 1H), 8.19–8.12 (m, 2H), 7.40–7.33 (m, 2H), 5.00–4.95 (m, 1H), 3.41–3.34 (m, 1H), 2.85 (dd, J = 17.4, 6.2, 1.5 Hz, 1H), 2.77 (dd, J = 17.5, 8.1, 1.6 Hz, 1H), 2.42–2.25 (m, 2H), 1.65 (br. s, 3H), 1.52 (br. s, 3H) ppm. Isolated signals of the minor regioisomer: δ = 9.59 (t, J = 1.5 Hz, 1H), 5.78 (dd, J = 17.4, 10.7 Hz, 1H), 5.10 (dd, J = 10.8, 1.1 Hz, 1H), 3.27 (dd, J = 9.6, 4.9 Hz, 1H) 0.98 (s, 3H), 0.95 (s, 3H) ppm. 13C NMR (126 MHz, CDCl3, major regioisomer): δ = 200.49, 151.93, 146.85, 135.18, 128.52 (2C), 123.93 (2C), 120.58, 49.13, 40.19, 34.95, 25.87, 18.01 ppm.

HRMS (ESI): m/z calculated for [C15H19NNaO2]+ [M+CH3OH+Na]+: 302.1363; found: 302.1377.

(S)-3-(4-Chlorophenyl)-6-methylhept-5-enal (3J)
Prepared according to general procedure E using trimethyl(3-methylbut-2-en-1-yl)silane 2a (0.1 mmol, 19.0 μL), 3-(4-chlorophenyl)acrylaldehyde 1e (0.13 mmol, 21.7 mg), aminocatalyst A (0.02 mmol, 14.1 mg) and 200 μL of a 0.15 M solution of trifluoroacetic acid (30 mol%) in 1,2-dichloroethane/acetonitrile 1:1. Time of irradiation 22 hours. The crude mixture was purified by flash column chromatography (hexane/dichloromethane, 80:20) to afford the product as a white waxy solid (8.8 mg, 37% yield, 79:21 mixture of regioisomers). The enantiomeric excess of the corresponding 2,4-dinitrophenylhydrazone (obtained upon condensation with 2,4-dinitrophenylhydrazine) was determined to be 78:22 for the major regioisomer by UPC analysis on a Daicel Chiralpak ID-3 column (eluent: 100% CO2 for 1 min, gradient 100% - 80% CO2 in iPrOH for 5 min, 80% CO2 in iPrOH for 2 min, gradient 80% - 100% CO2 in iPrOH for 1 min; flow rate 2.0 mL/min, λ = 344 nm. Major regioisomer: τMajor = 8.40 min, τMinor = 8.19 min.

[α]D h = -0.4 (c = 0.3, CHCl3, 79:21 rr, 78:22 er).

1H NMR (500 MHz, CDCl3, major regioisomer): δ = 9.65 (t, J = 1.9 Hz, 1H), 7.28–7.23 (m, 2H), 7.15–7.10 (m, 2H), 5.02–4.93 (m, 1H), 3.24–3.17 (m, 1H) 2.75 (dd, J = 16.9, 6.4, 1.9 Hz, 1H), 2.67 (dd, J = 16.8, 8.2, 2.0 Hz, 1H), 2.35–2.21 (m, 2H), 1.65 (br. s, 3H), 1.52 (br. s, 3H) ppm. Isolated signals of the minor regioisomer: δ = 9.54 (t, J = 1.9 Hz, 1H), 5.78 (dd, J = 17.5, 10.8 Hz, 1H), 5.06 (dd, J = 10.8, 1.2 Hz, 1H), 3.10 (dd, J = 9.1, 5.9 Hz, 1H), 0.95 (s, 3H), 0.93
(S, 3H) ppm. $^{13}$C NMR (126 MHz, CDCl$_3$, major regioisomer): $\delta = 201.83, 146.13, 142.79, 132.60, 131.19, 129.19$ (2C), 129.06 (2C) 121.49, 49.66, 40.20, 35.54, 26.13, 18.25 ppm.

HRMS (ESI): Since 3u could not be detected directly, detection of the corresponding dinitrophenyl hydrazone was successful: m/z calculated for [C$_{20}$H$_{21}$Cl$_4$NaO$_4$]$^+$ [M+Na]$^+$: 439.1144; found: 439.1149.

(S)-5-(Cyclohex-1-en-1-yl)-3-phenylpentan-1-ol (5b)

Aldehyde 3b (1 equiv., 50 μmol, 12.0 mg) was dissolved in a vial in MeOH (HPLC grade, 1.2 mL). After cooling to 0 °C, NaBH$_4$ (2 equiv., 0.1 mmol, 3.8 mg) was added and the ice bath removed. After stirring for 1 h, the mixture was concentrated under reduced pressure, redissolved in DCM (1 mL) and filtered over a short plug of silica gel by afterwashing with DCM (10 mL). The filtrate was concentrated to yield the alcohol 4b (with traces of branched 4b' with a regioisomeric ratio of $= 96:4$) which was used without further purification ($^1$H NMR in Figure S6, top spectra).

The crude alcohol 4b (1 equiv., 50 μmol) was then redissolved in a dry vial in DCE (anhydrous, 1.2 mL). p-TsOH (0.2 equiv., 10 μmol, 1.9 mg) and Zn(OTf)$_2$ (0.2 equiv., 10 μmol, 3.6 mg) were added and the reaction was stirred for 6 h at room temperature. The mixture was filtered through a short plug of silica gel and concentrated under reduced pressure. The crude $^1$H-NMR (Figure S7, middle spectra) revealed the presence of 5a accompanied with small amounts of 4b/4b' (5b/4b/4b' = 84:1:5).

In order to determine if this was the final equilibria, the mixture was subjected again to the isomerization conditions (as described above) for another 2 h at room temperature. Final purification of the product by flash chromatography (silica gel, DCM:hexane = 50:50) afforded 8.7 mg (72%) of alcohol 5b accompanied by 4b/4b' with unchanged composition (5b/4b/4b' = 84:11:5) as observed before. $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 7.31$ - 7.26 (m, 2H), 7.21 - 7.14 (m, 3H), 5.32 (bs, 1H), 3.58-3.42 (m, 2H), 2.70 - 2.63 (m, 1H), 1.98 - 1.91 (m, 3H), 1.88-1.65 (m, 7H), 1.61-1.49 (m, 4H) ppm. $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta = 145.20, 137.71, 128.58$ (2C), 127.83 (2C), 126.31, 120.99, 61.40, 42.35, 39.80, 35.99, 35.03, 28.51, 25.37, 23.15, 22.72 ppm.

HRMS (APCI): m/z calculated for [C$_{17}$H$_{25}$]+ [M+H-H$_2$O]$^+$: 227.1793; found: 227.1794.

Figure S6: $^1$H NMR spectra of crude 4b (top blue, 500 MHz), isomerization to 5b after 6h (middle, red, 400 MHz) and after additional 2h (bottom, green, 500 MHz).
Figure S7: Zoom on the olefinic signals (1H NMR spectrum, 500 MHz) of crude 4b (top, blue), revealing a ratio of 4b:4b' = 96:4. The 2 spectra below show the isomerized product 5b revealing a ratio of 5b:4b:4b' = 84:11:5 after 6h (middle red, 400 MHz) and an unchanged composition of the same mixture after additional 2h reaction time (bottom, green, 500 MHz).

5 Mechanistic Studies

5.1 Quantum Yield Determination

A ferrioxalate actinometer solution was prepared by following the Hammond variation of the Hatchard and Parker procedure\textsuperscript{(17)} outlined in the Handbook of Photochemistry.\textsuperscript{(18)} Ferrioxalate actinometer solution measures the decomposition of ferric ions to ferrous ions, which are complexed by 1,10-phenanthroline and monitored by UV/Vis absorbance at 510 nm. The moles of iron-phenanthroline complex formed are related to moles of photons absorbed. The values of the quantum yield of potassium ferrioxalate are related to concentration and wavelength.

The solutions were prepared and stored in the dark (red light):

1. **Potassium ferrioxalate solution 0.012M**: 147.4 mg of potassium ferrioxalate (commercially available from Alfa Aesar) and 69.5 μL of sulfuric acid (96%) were added to a 25 mL volumetric flask, and filled to the mark with water (HPLC grade).
2. **Phenanthroline solution**: 0.2% by weight of 1,10-phenanthroline in water (100 mg in 50 mL volumetric flask or 50 mg in 25 mL).
3. **Buffer solution**: to a 100 mL volumetric flask 4.94 g of NaOAc and 1.0 mL of sulfuric acid (96%) were added and filled to the mark with water (HPLC grade).
4. **Internal standard solution**: 1.052 g of 1,3,5-trimethoxybenzene was added to a 5 mL volumetric flask which was filled up with HPLC grad acetonitrile (1.25 M).

Reaction setup:

1. **Reaction solution**: A 8 mL flame-dried and argon-purged glass vial with stir bar was charged with allyl silane 2c (1 equiv., 0.1 mmol, 18.4 mg) and amine catalyst C (20 mol%, 0.02 mmol, 14.1 mg). The vial was further flushed with argon, then enal 1a (1.3 equiv., 0.13 mmol, 16.4 μL) and 200 μL of an argon-sparged 0.15 M acetonitrile and 1,2-dichloroethane (1:1) solution of TFA (30 mol%, 0.03 mmol, 11.5 μL) were added. The vial was then put in the HP-LED 420 nm at 1 cm distance at -15 °C with irradiance of 112±2 mW/cm². Four different reactions were setup and irradiated for different times: 25
min, 50 min, 75 min and 100 min. After each reaction was finished, internal standard solution (500 μL, 0.625 mmol) was added. This solution was then diluted with 300 μL of acetonitrile (HPLC grade) and analyzed by GC-FID.

2. **Actinometer solutions**: A 8 mL glass vial was loaded with 1.0 mL of actinometer solution and placed on the 420 nm HP-LED with the same light intensity as the reaction. Four different actinometer solutions were irradiated in sequence for 3 s, 6 s, 9 s and 12 s. To irradiate the vial, it was placed on the holder with the light off and the light was turned on for the desired time. After each irradiation the actinometer solutions were carefully transferred into a 10 mL volumetric flask, then 0.5 mL of phenanthroline solution and 2.0 mL of buffer solution were added and the flask was filled up with water (HPLC grade). The mixture was then analysed by UV-Vis (Figure S8).

![Actinometer Solution irradiated](image)

**Figure S8.** UV-Vis recorded spectra of the actinometer solutions irradiated for different periods of times.

The moles of Fe2+ formed for each sample are determined using Beers’ Law (Eq. 1):

\[
\text{Moles of Fe(II)} = \frac{V_1 V_2 \Delta A(510 \text{ nm})}{10^3 V_2 l \varepsilon(510 \text{ nm})} \tag{Eq. 1}
\]

where \(V_1\) is the irradiated volume (1 mL), \(V_2\) is the aliquot of the irradiated solution taken for the determination of the ferrous ions (1 mL), \(V_3\) is the final volume after complexation with phenanthroline (10 mL), \(l\) is the optical path-length of the irradiation cell (1 cm), \(\Delta A(510 \text{ nm})\) is the optical difference in absorbance between the irradiated solution and the one stored in the dark, \(\varepsilon(510 \text{ nm})\) is the extinction coefficient of the complex Fe(phen)_3^{2+} at 510 nm (11100 L mol\(^{-1}\) cm\(^{-1}\)). The moles of Fe^{2+} formed (\(x\)) are plotted as a function of time (t) (Figure S9). The slope of this line was correlated to the moles of incident photons by unit of time (\(q_{n,p}\)) by the use of the following Equation 2:

\[
\Phi(\lambda) = \frac{dx/dt}{q_{n,p}[1 - 10^{-\Delta A(\lambda)}]} \tag{Eq. 2}
\]

where \(dx/dt\) is the rate of change of a measurable quantity (spectral or any other property), the quantum yield (\(\Phi\)) for Fe^{2+} at 416 nm is 1.12 \(^{[19]}\), \([1-10^{-\Delta A(\lambda)}]\) is the ratio of absorbed photons by the solution, and \(A(\lambda)\) is the absorbance of the actinometer at the wavelength used to carry out the experiments (420 nm). The absorbance at 420 nm (\(A(420)\)) was 1.08.
The photon flux, which is \( q_0^{n,p} \), was determined to be 1,52514x10^{-7} \text{ einstein s}^{-1}. The moles of product per unit of time are plotted against the number of photons absorbed (Figure S10). The photons absorbed are correlated to the number of incident photons by the use of Equation 2.

According to this, if we plot the moles of product (x-axis) versus the moles of incident photons (\( q_0^{n,p} \text{dt} \)), the slope is equal to:

\[
\text{slope} = \Phi \left[ 1 - 10^{-A(420 \text{ nm})} \right]
\]

(Eq. 3)

where \( \Phi \) is the quantum yield to be determined and \( A(420 \text{ nm}) \) is the absorption of the reaction under study. \( A(420 \text{ nm}) \) was measured to be of 0.229 for the model reaction mixture.

The quantum yield of the conjugate allylation of \( 2c \) with cinnamaldehyde was calculated to be 0.005.
5.2 Cyclic Voltammetry Studies

**Figure S2.** Cyclic voltammogram of Allyl Silane 2a [0.03 M] in [0.1 M] TBAPF$_6$ in CH$_3$CN. Sweep rate: 70 mV/s. Pt electrode working electrode, Ag/AgCl (NaCl saturated) reference electrode, Pt wire auxiliary electrode. Irreversible oxidation, $E_{pA} = E_{ox}(2a^+/2a) = +1.7$ V; $E_{pA}$ is the anodic peak potential.

**Figure S3.** Cyclic voltammogram of Allyl Silane 2b [0.03 M] in [0.1 M] TBAPF$_6$ in CH$_3$CN. Sweep rate: 70 mV/s. Pt electrode working electrode, Ag/AgCl (NaCl saturated) reference electrode, Pt wire auxiliary electrode. Irreversible oxidation, $E_{pA} = E_{ox}(2b^+/2b) = +1.4$ V; $E_{pA}$ is the anodic peak potential.
5.3 UV/Vis absorption spectrum of iminium salt

Figure S4. Absorption spectra of the preformed iminium ion (as BF₄ salt) at different concentrations in CH₃CN. The wavelength of maximum absorbance is 363 nm. The tail wavelength was considered to be at about 435 nm.

5.4 On-off experiment

We performed a light on/light off experiment with cinnamaldehyde 1a and silane 2d according to our standard procedure. Aliquots (50 μL) were taken from the same reaction mixture (0.15 mmol scale, 300 μL of DCE/MeCH (1:1) as solvent, volumes of reagents omitted) and product formation was determined by concentration in vacuo followed by ¹H NMR analysis of the crude mixture using trichloroethylene as the internal standard. A clear off-period was observed, which indicates that light is necessary to trigger the reaction.

Figure S5. Experiment used for an on-off study, conducted under our standard conditions.
6 X-ray Crystallographic Data

Single Crystal X-ray Diffraction Data for compound 3i

Crystals of the compound 3i were obtained by slow evaporation of a diethyl ether / n-hexane solution (1:1). Data Collection. Measurements were made on a Bruker-Nonius diffractometer equipped with an APPEX 2 4K CCD area detector, a FR591 rotating anode with MoKα radiation. Montel mirrors and a Cryostream Plus low temperature device (T = 100K). Full-sphere data collection was used with ω and φ scans.

Supplementary Table 1. Crystal data and structure refinement for 3i. CCDC 2105317

| Property                      | Value                      |
|-------------------------------|----------------------------|
| Empirical formula            | C17 H21 N O3               |
| Formula weight               | 287.35                     |
| Temperature                  | 100(2)K                    |
| Wavelength                   | 1.54178 Å                  |
| Crystal system               | monoclinic                 |
| Space group                  | P 21                       |
| Unit cell dimensions         | a = 6.1037(6)Å             |
|                             | b = 8.5699(8)Å             |
|                             | c = 14.7260(14)Å           |
| Volume                       | 754.96(13) Å³              |
| Z                             | 2                          |
| Density (calculated)         | 1.264 Mg/m³                |
| Absorption coefficient       | 0.696 mm⁻¹                 |
| F(000)                       | 308                        |
| Crystal size                 | 0.500 x 0.500 x 0.030 Å³   |
| Theta range for data collection | 3.062 to 67.894°         |
Index ranges  -7<=h<=7, -10<=k<=10, -17<=l<=16
Reflections collected  8743
Independent reflections 2681\[R(int) = 0.0288]\]
Completeness to theta =67.894° 99.2%
Absorption correction  Multi-scan
Max. and min. transmission  0.75 and 0.56
Refinement method  Full-matrix least-squares on F^2
Data / restraints / parameters  2681/ 1/ 190
Goodness-of-fit on F^2  1.075
Final R indices [I>2\textsigma(I)]  R1 = 0.0283, wR2 = 0.0736
R indices (all data)  R1 = 0.0285, wR2 = 0.0738
Flack parameter  x =0.05(6)
Largest diff. peak and hole   0.125 and -0.191 e.Å^-3
7 References

[1] M. Silvi, C. Verrier, Y. P. Rey, L. Buzzetti, P. Melchiorre Nat. Chem. 2017, 9, 868–873.
[2] G. Battistuzzi, S. Cacchi, G. Fabrizi Org. Lett. 2003, 5, 777–780.
[3] P. Bonilla, Y. P. Rey, C. M. Holden, P. Melchiorre Angew. Chem. Int. Ed. 2018, 57, 12819–12823.
[4] A. Gontala, S. K. Woo Adv. Synth. Catal. 2020, 362, 3223–3228. See also: Y. Tsuji, M. Funato, M. Ozawa, H. Ogiyama, S. Kajita, T. Kawamura J. Org. Chem. 1996, 61, 5779–5787.
[5] N. Selander, J. R. Paasch, K. J. Szabó J. Am. Chem. Soc. 2011, 133, 409–411.
[6] B. Schmidt J. Org. Chem. 2004, 69, 7672–7687.
[7] M. Gensini, M. Altamura, T. Dimoulas, V. Fedi, D. Giannotti, S. Giuliani, A. Guidi, N. J. S. Harmat, S. Meini, R. Nannicini, F. Pasqui, M. Tramontana, A. Triolo, C. A. Maggi ChemMedChem 2010, 5, 65–78.
[8] Y. Masuda, M. Hoshi, A. Arase Bull. Chem. Soc. Jpn. 1992, 65, 3294–3299.
[9] S. Denmark, M. Harmata, K. White J. Org. Chem. 1987, 15, 4031–4042.
[10] C. Morrill, R. H. Grubbs J. Am. Chem. Soc. 2005, 127, 2842–2843.
[11] R. E. Kyne, M. C. Ryan, L. T. Kliman J. P. Morken, Org. Lett. 2010, 12, 3796–3799.
[12] D. Chen, Y. Zhang, X. Pan, F. Wang, S. Huang Adv. Synth. Catal. 2018, 360, 3607–3612
[13] D. Tzeng, W. P. Weber J. Org. Chem. 1981, 46, 265–267.
[14] L. Lu, J. C. Siu, Y. Lai, S. Lin J. Am. Chem. Soc. 2020, 142, 21272–21278.
[15] J. I. Yoshida, K. Muraki, H. Funahashi, N. Kawabata J. Org. Chem. 1986, 51, 3996–4000.
[16] D. M. Hodgson, M. J. Fleming, S. J. Stanway J. Org. Chem. 2007, 72, 4763–4773
[17] C. G. Hatchard, C. A. Parker Proc. R. Soc. (London), 1956, A235, 518.
[18] M. Montalti, A. Credi, L. Prodi, M. T. Gandolfi Handbook of photochemistry, Taylor&Francis, 2006, 601
[19] E. E. Wegner, A. W. Adamson J. Am. Chem. Soc. 1966, 86, 394–404.
7  NMR spectra of new compounds

7.1  Starting material precursor

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{19}$F NMR (376 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{19}\text{F NMR}$ (376 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{19}$F NMR (376 MHz, CDCl$_3$)

\[ \text{Structure Image} \]
7.2 Starting material silanes

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)

$^1$C NMR (126 MHz, CDCl$_3$)
7.3 Products NMR spectra

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)

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$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{19}$F NMR (376 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{19}$F NMR (376 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{19}$F NMR (376 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
8 UPC² traces

Full trace for 3a racemic:

Full trace for 3a enantioenriched:

Trace (Zoom) for 3a racemic:

Trace (Zoom) for 3a enantioenriched:
Full trace for 3b racemic:

[Graph Image]

Full trace for 3b enantioenriched:

[Graph Image]

Trace (Zoom) for 3b racemic (Zoom):

[Graph Image]

Full trace for 3b enantioenriched (Zoom):

[Graph Image]
Full trace for 3c racemic:

Full trace for 3c enantioenriched:

Trace (Zoom) for 3c racemic:

Trace (Zoom) for 3c enantioenriched:
Full trace for 3d racemic:

Trace (Zoom) for 3d racemic:

Full trace for 3d enantioenriched:

Trace (Zoom) for 3d enantioenriched:
Full trace for 3e racemic:

Trace (Zoom) for 3e racemic:

Full trace for 3e enantioenriched:

Trace (Zoom) for 3e enantioenriched:
Full trace for 3f racemic:

Full trace for 3f enantioenriched:

Trace (Zoom) for 3f racemic:

Trace (Zoom) for 3f enantioenriched:
Full trace for 3g racemic:

Full trace for 3g enantioenriched:

Trace (Zoom) for 3g racemic:

Trace (Zoom) for 3g enantioenriched:
Full trace for 3h racemic:

Full trace for 3h enantioenriched obtained using (E)-silane:

Full trace for 3h enantioenriched obtained using (Z)-silane:

Trace (Zoom) for 3h racemic:

Trace (Zoom) for 3h enantioenriched obtained using (E)-silane:

Trace (Zoom) for 3h enantioenriched obtained using (Z)-silane:
Full trace for $3i$ racemic:

Full trace for $3i$ enantioenriched:

Trace (Zoom) for $3i$ racemic:

Trace (Zoom) for $3i$ enantioenriched:
Full trace for 3j racemic:

Full trace for 3j enantioenriched:

Trace (Zoom) for 3j racemic:

Trace (Zoom) for 3j enantioenriched:
Full trace for 3k \textit{racemic}:

![Graph showing a full trace for 3k racemic.]

Full trace for 3k enantioenriched:

![Graph showing a full trace for 3k enantioenriched.]

Trace (Zoom) for 3k \textit{racemic}:

![Graph showing a zoomed trace for 3k racemic.]

Trace (Zoom) for 3k enantioenriched:

![Graph showing a zoomed trace for 3k enantioenriched.]

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Full trace for 3l racemic:

Full trace for 3l enantioenriched:

Trace (Zoom) for 3l racemic:

Trace (Zoom) for 3l enantioenriched:
Full trace for 3m racemic:

Full trace for 3m enantioenriched:

Trace (Zoom) for 3m racemic:

Trace (Zoom) for 3m enantioenriched:
Full trace for 3n racemic:

![Full trace for 3n racemic](image1.png)

Full trace for 3n enantioenriched:

![Full trace for 3n enantioenriched](image2.png)

Trace (Zoom) for 3n racemic:

![Trace (Zoom) for 3n racemic](image3.png)

Trace (Zoom) for 3n enantioenriched:

![Trace (Zoom) for 3n enantioenriched](image4.png)
Full trace for **3p racemic**:  

![Full trace for 3p racemic](image)

Full trace for **3p enantioenriched**:  

![Full trace for 3p enantioenriched](image)

Trace (Zoom) for **3p racemic**:  

![Trace (Zoom) for 3p racemic](image)

Trace (Zoom) for **3p enantioenriched**:  

![Trace (Zoom) for 3p enantioenriched](image)
Full trace for 3q racemic:

Trace (Zoom) for 3q racemic:

Full trace for 3q enantioenriched:

Trace (Zoom) for 3q enantioenriched:
Full trace for 3r racemic:

Full trace for 3r enantioenriched:

Trace (Zoom) for 3r racemic:

Trace (Zoom) for 3r enantioenriched:
Full trace for 3s racemic:

Full trace for 3s enantioenriched:

Trace (Zoom) for 3s racemic:

Trace (Zoom) for 3s enantioenriched:
Full trace for $3t$ racemic:

Full trace for $3t$ enantioenriched:

Trace (Zoom) for $3t$ racemic:

Trace (Zoom) for $3t$ enantioenriched:
Full trace for 3u racemic:

Full trace for 3u enantioenriched:

Trace (Zoom) for 3u racemic:

Trace (Zoom) for 3u enantioenriched: