Materials and methods

All reactions were carried out under positive pressure of argon unless otherwise noted. Phenylsilane was purchased from Oakwood Chemicals and used without further purification. Solutions of tert-butyl hydroperoxide (TBHP) were prepared using the stated procedures stated below from solutions purchased from Sigma Aldrich. Anhydrous isopropanol was first dried over activated molecular sieves (4 Å) overnight then distilled from calcium hydride (10 % w/v) under positive pressure of nitrogen.

Pentane, hexanes, dichloromethane (DCM), toluene, ethyl acetate (EtOAc), and diethyl ether were purchased from Fisher Chemicals and used without further purification. Benzene, dimethylsulfoxide (DMSO), methanol (MeOH), N-dimethylformamide (DMF), dichloroethane (DCE), α, α, α-trifluorotoluene and triethylamine were purchased from Sigma Aldrich, EMD Chemicals, Fisher Chemicals or Acros Organics and used without further purification. Anhydrous dichloromethane was distilled from calcium hydride (10 % w/v) under positive pressure of nitrogen. Anhydrous tetrahydrofuran (THF) was distilled over sodium/benzophenone ketyl under positive pressure of nitrogen. All other anhydrous solvents were purchased from Fisher Chemicals, Sigma Aldrich or Acros Organics and used without further purification, unless otherwise stated. All other reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated.

Reactions were monitored by thin layer chromatography (TLC) with precoated silica gel plates from EMD Chemicals (TLC Silica gel 60 F254, 250 µm thickness) using UV light as the visualizing agent and an acidic mixture of anisaldehyde, phosphomolybdic acid (PMA), chromic acid, iodine vapor, or basic
aqueous potassium permanganate (KMnO₄), and heat as developing agents. Preparatory thin layer chromatography (PTLC) was performed using the aforementioned silica gel plates. Flash column chromatography was performed over silica gel 60 (particle size 0.035-0.07 mm) from Acros Organics. NMR spectra were recorded on Bruker DRX-600 (equipped with a Cryoprobe), DRX-500 or DPX-400 and calibrated using residual non-deuterated solvent as an internal reference (CHCl₃ @ 7.26 ppm ¹H NMR, 77.16 ppm ¹³C NMR). The following abbreviations (or combinations thereof) were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. LC/MS analysis was performed on Agilent 1100 series HPLC/MSD A61946D system with ACN and 0.01% TFA in H₂O as eluents. GC/MS analysis was performed on Agilent 7820A/5975 GC/MSD system with helium as a carrier gas. Unless otherwise specified, GC runs were preformed with the following method: GC/MS; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 200 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min.

**Experimental procedures**

**1. Model procedure for hydrogenation**

To a stirring solution of olefin (1.0 equiv.) in anhydrous solvent [Note 1] (0.50 M [Note 2] with respect to olefin substrate) under argon, add phenylsilane (1.0 equiv.) and a solution of TBHP [Note 3] (1.5 equiv.). Degas the resulting mixture for 10 minutes by bubbling argon through the solution. Afterwards, add the metal catalyst [Note 1] (0.1 equiv.) and further degas the mixture for another 30 seconds [Note 4]. At 0.5 M, reactions are generally complete between 30 minutes to 2 hours. Once the reaction is complete, evaporate the isopropanol and load the crude mixture directly onto silica for purification via column chromatography. An optional aqueous workup with ammonium hydroxide can be performed if necessary (ex. for relative reactivity studies) – quench the reaction with ammonium hydroxide (1mL), extract with ethyl acetate (x3), wash with brine, dry with MgSO₄ and concentrate to give the crude mixture.

[Note 1] **Solvents and catalysts:**

General observations: Mn(dpm)₃ and isopropanol is the optimal catalyst/solvent combination for this reaction. If solubility in isopropanol is an issue, up to 20% of THF and DCM can be added with minimal effect on the reaction. Alternatively, Co(dpm)₂ can be used as a catalyst and the reaction will tolerate a wider range of solvents – isopropanol, DCM, DCE or α, α, α-trifluorotoluene (pentane, hexanes and THF can also be used, but will lead to lower yield and selectivity). However, under the same conditions, reactions catalyzed by Co(dpm)₂ are generally slower and may require higher catalyst loading compared to those catalyzed by Mn(dpm)₃.

Procedures used to prepare the catalysts:

**Mn(dpm)₃** (DPM: DPM-2,2,6,6-tetramethyl-3, 5-heptanedionato-)

- Method A: To a vigorously stirring mixture of manganese (II) sulfate monohydrate (1.5 g, 9 mmol, 1.0 equiv.) and 2,2,6,6-tetramethyl-3,5-heptanedione (5.0 g, 27 mmol, 4.0 equiv.) in a mixture of water (30 mL) and methanol (6 mL) at room temperature was added NH₄OH (50% v/v)
(12 mL) dropwise, resulting in the immediate formation of a dark olive green/brown precipitate. The precipitate was filtered off, washed with water (3x10 mL) and dried in vacuo for 24 hours to give Mn(dpm)$_3$ (4.9 g) in 90% yield.

- Method B$^{35}$: 2,2,6,6-tetramethyl-3,5-heptanedione (2.6 ml, 12.0 mmol, 3.0 equiv.) was added to a solution of manganese (II) diacetate tetrahydrate (1.0 g, 4.0 mmol, 1.0 equiv.) in methanol (9 ml) under air and the resulting yellow-green solution was stirred at 23°C. A solution of sodium hydroxide (0.5 g, 12.0 mmol, 3.0 equiv.) in water (2.4 ml, deionized) was then added and a green solid immediately precipitated. After diluting with methanol (11 ml), the reaction mixture was stirred at 23°C under air for 13 hours and then filtered. The green-brown solid was dried under a high vacuum at 60°C for 4 hours and then dissolved in hot isopropanol (30 ml). Mn(dpm)$_3$ precipitated partially upon cooling, and the precipitation was completed by adding water (3 ml). The suspension was filtered and the resulting olive green solid was dried under high vacuum for 12 hours to give Mn(dpm)$_3$ as a dark green powder (0.76 g, 1.2.0 mmol) in 62% yield.

Co(dpm)$_2$

- To a degassed solution of 2,2,6,6-tetramethyl-3,5-heptanedione (4.17 ml, 20 mmol, 2.0 equiv.) in water (21 ml) at 65°C was added Co(II)Cl$_2$ (1.3 g, 10 mmol, 1.0 equiv.) and the solution turned pink-red. To this solution was quickly added a solution of NaOH (0.80 g, 20 mmol, 2.0 equiv.) in water (7 ml). Thick blue-purple precipitate formed immediately, but the solution was stirred at 65°C for 3 more hours to ensure complete precipitation. The mixture was then cooled to room temperature and filtered. The collected solid was dissolved in a minimum amount of Et$_2$O and filtered through a plug of Celite. The solution was the nevaporated to yield a pink solid, which was dried under high vacuum until the solid turned a deep homogenous purple color.$^{36}$

[Note 2] Solvent concentration:

The reaction tolerates a range of concentrations, from 0.05 M to 0.5 M. The reaction speeds up considerably with increasing concentration, and thus 0.5 M was chosen to be the optimal concentration for ease of preparation. Any increase in concentration beyond 0.5 M causes the catalysts to have solubility issues. Caution: at 0.5 M with 10 mol% catalyst, 1.0 equiv. PhSiH$_3$ and 1.5 equiv. TBHP, the reaction is slightly exothermic (cooling is detrimental to the reaction). The higher the catalyst, PhSiH$_3$ or TBHP loading, the more exothermic the reaction will be.

[Note 3] TBHP solutions:

General observations: TBHP can be added as a solution in a variety of different solvents in this reaction. The anhydrous 5.5 M TBHP solution in decane (commercially available) is generally used due to its ready accessibility. However, if decane is incompatible (ex. volatile and non-polar substrates), TBHP in other solvents (hexanes, pentane, DCM), prepared via the procedures below, can be used instead.

Procedure used to prepare TBHP solutions:
To a solution of brine (1 mL) and 70% aq. solution of TBHP (10 mL) in a separatory funnel was
added the desired solvent (hexanes, pentane, DCM, etc., 10 mL). The mixture was then shaken
and the two layers were left to settle for 10 minutes. If at this point an emulsion was still present,
an additional 1 mL of brine was added and the mixture was shaken again. When a clear separation of the organic and aqueous phases was observed, the organic layer was collected and
dried over MgSO₄. The resulting clear solution was then filtered and stored over activated 4 Å
molecular sieves and stored at -4 °C. The exact concentration of the TBHP solution was
determined by NMR integration of TBHP resonances relative to those of the solvent.

[Note 4] Degassing:
Degassing for more than 30 seconds after addition of catalyst will be detrimental to the reaction.

2. Optimization results for Hydrogenation

![Chemical structure](image)

**Conditions**

| Radical | 10 mol% Mn(dpm)₃, 1.0 equiv. PhSiH₃, 1.5 equiv. TBHP, i-PrOH (0.5 M), 1 h | 85% 84 : 16 |
| Change from optimized Procedure A |
| Entry 1 No TBHP | 10% 87 : 13 |
| Entry 2 Et₃SiH instead of PhSiH₃ – no reaction | – – |
| Entry 3 10 mol% Mn(acac)₃ | 10% 90 : 10 |
| Entry 4 10 mol% Co(acac)₂ at 22 °C | 46% 89 : 11 |
| Entry 5 THF instead of i-PrOH | 13% 87 : 13 |
| Entry 6 10 mol% Co(dpm)₂ | 69% 86 : 14 |
| Entry 7 5 equiv. H₂O | 36% 85 : 15 |

Table 1. A sample of optimization results.

General procedure for experiments in Table 1 (see entries 1-7 for different modifications made to
this procedure): The starting olefin 10 (30.5 mg, 0.2 mmol, 1.0 equiv) was dissolved in anhydrous iPrOH
(0.40 mL, 0.5 M) under argon. To this stirring solution, phenylsilane (24 µL, 1.0 equiv.), decane (39 µL,
0.20 mmol, 1.0 equiv.) and an 8.0 M solution of TBHP in hexanes (37.5 µL, 0.3 mmol, 1.5 equiv.) were
added and the resulting mixture was degassed by bubbling argon through the solution for 10 minutes.
Mn(dpm)₃ (12 mg, 0.02 mmol, 10 mol%) was then added in one portion and the reaction was then further
degassed for an additional 30 seconds. After 60 minutes, a small aliquot of the reaction mixture was
quenched with an aqueous NH₄OH solution (1:1 v/v) and analyzed by GC-MS (GC/MSD; HP-5MS UI; 139
KPa; flow rate 2 mL/min; inlet temperature 200 °C; column temperature 50 °C for 0 min, then 20 °C/min to
280 °C, then hold 2 min).
All the yields and ratios in this table were obtained by GC-MS analysis. Since the ratio of 11 and 12 determined by GC-MS integration was found to be identical to that determined by quantitative $^{13}$C NMR, the ratios in this table were only analyzed by GC-MS. The yields were also determined by GC-MS analysis using decane as an internal standard, which was first calibrated against the relative GC-MS integration of an 11:12:decane mixture (42:8:50 by mass) to correct for differences in GC-MS response factors.

3. General Procedures

Procedure A: [Mn(dpm)$_3$]

The starting olefin (0.50 mmol, 1.0 equiv.) was dissolved in anhydrous iPrOH (1.0 mL, 0.5 M) under argon. To this stirring solution were added phenylsilane (61 µL, 1.0 equiv.) and TBHP (1.5 equiv.) and the resulting mixture was degassed by bubbling argon through the solution for 10 minutes. Mn(dpm)$_3$ (30 mg, 0.05 mmol, 10 mol%) was then added in one portion and the reaction was then degassed for an additional 30 seconds. Once the reaction was judged to be complete (by GCMS or LCMS via complete consumption of starting material), the iPrOH was evaporated and the crude mixture was loaded directly onto a silica column for purification to obtain the desired saturated product.

Procedure B: [Co(dpm)$_2$]

The starting olefin (0.5 mmol, 1.0 equiv.) was dissolved in anhydrous solvent (iPrOH/DCE/α,α,α-trifluorotoluene, 1mL, 0.5 M) under argon. To this stirring solution were added phenylsilane (61 µL, 1.0 equiv.) and TBHP (1.5 equiv) and the resulting mixture was degassed by bubbling argon through the solution for 10 minutes. Co(dpm)$_2$ (18.5 mg, 0.05 mmol, 10 mol%) was then added in one portion and the reaction was then further degassed for an additional 30 seconds. Once the reaction was judged to be complete (by GCMS or LCMS via complete consumption of starting material), the solvent was evaporated and the crude mixture was loaded directly onto a silica column for purification to obtain the desired saturated product.

10: The title compound was prepared according to a previously reported procedure.$^{37}$ The spectral data collected matched those previously reported.$^{37}$

11: Using procedure A with the following modifications gave the title compound (27.4 mg, 0.18 mmol) as a mixture of diastereomers (6.6:1 trans: cis) as a colorless liquid in 71% yield:

- Starting olefin 10 (38.0 mg, 0.25 mmol, 1.0 equiv.)
- Anhydrous iPrOH (0.50 mL, 0.5 M)
- Phenylsilane (31 µL, 0.25 mmol, 1.0 equiv.)
- 5.5 M of TBHP in pentane (73 µL, 0.38 mmol, 1.5 equiv.)
- Mn(dpm)$_3$ (15.0 mg, 0.025 mmol, 10 mol%)
- Due to volatility, the crude reaction mixture was not evaporated but was instead loaded directly onto silica (30 g)
- Column solvent: pentane

| H NMR (400 MHz, CDCl$_3$)        | 13C NMR (101 MHz, CDCl$_3$) | GCMS (EI, 70 eV) m/z (%) |
|-----------------------------------|-----------------------------|-------------------------|
| 1.72 (d, J = 8.6 Hz, 3 H)         | 48.08                       | 154 (1)                 |
| 1.53-1.43 (m, 1 H)                | 36.08                       | 152 (1)                 |
| 1.34-1.16 (m, 2 H)                | 33.02                       | 139 (4)                 |
| 1.03-0.81 (m, 16 H)               | 32.55                       | 137 (42)                |
|                                   | 27.78                       | 109 (1)                 |
|                                   | 27.56                       | 97 (42)                 |
|                                   | 22.87                       | 96 (46)                 |
|                                   |                              | 83 (23)                 |
|                                   |                              | 81 (35)                 |
|                                   |                              | 69 (21)                 |
|                                   |                              | 67 (15)                 |
|                                   |                              | 57 (77)                 |
|                                   |                              | 56 (100)                |
|                                   |                              | 55 (69)                 |

TLC
R$_f$ = 0.95 hexane
(chromic acid stain)

13b: Aluminum trichloride (134 mg, 1.0 mmol, 0.1 equiv.) was added to a stirring, neat solution of methyl vinyl ketone (0.91 ml, 10 mmol, 1.0 equiv.) and isoprene (2.0 ml, 20 mmol, 2.0 equiv.) at 0°C. After 30 min. the reaction was quenched with an ice-water mixture and diluted with dichloromethane (20 ml). The mixture was washed with sat. NaHCO$_3$ (20 ml) and extracted with dichloromethane (3 x 10 ml). The organic layers were then washed with brine (40 ml) and dried over K$_2$CO$_3$. After evaporation of the solvent at reduced pressure, the resulting crude yellow oil was purified by flash chromatography (hexane:EtOAc 9:1, R$_f$ = 0.60, yellow-green stain with p-anisaldehyde) and 2-methyl-2-(4-methylcyclohex-3-en-1-yl)-1,3-dioxolane was obtained as a colorless oil in 59% yield.
In a flask under nitrogen, TsOH (2.85 g, 15 mmol, 3.0 equiv.) was dried by azeotropically removing water with benzene three times. Ethylene glycol (1.4 ml, 25 mmol, 5.0 equiv.) and the ketone (690 mg, 5.0 mmol, 1.0 equiv.) was then added to the flask and the mixture was then dissolved in anhydrous benzene (30 mL). The resulting solution was heated at reflux overnight with a Dean-Stark trap attached. When the reaction was judged to be complete by GC analysis, the flask was then cooled and the mixture was diluted with dichloromethane (20 mL). The resulting solution was then poured onto sat. NaHCO₃ (40 ml), and the mixture was extracted with dichloromethane (3x 15 ml), washed with brine (70 ml), dried over K₂CO₃ and concentrated to yield the crude mixture. The crude mixture was then purified by flash chromatography (hexane/EtOAc 9:1 -> 8:2, Rᵣ = 0.6 yellow stain with p-anisaldehyde) to give the title compound as a slightly yellow oil in quantitative yield.

|       | ¹H NMR (400 MHz, CDCl₃) | ¹³C NMR (101 MHz, CDCl₃) | GCMS (EI, 70 eV) m/z (%) |
|-------|------------------------|--------------------------|--------------------------|
|       | 5.38 (s, 1 H)          | 134.00                   | 182 (2)                  |
|       | 3.98-3.88 (m, 4 H)     | 120.51                   | 167 (6)                  |
|       | 2.11-1.84 (m, 5 H)     | 111.90                   | 137 (2)                  |
|       | 1.77-1.72 (m, 1 H)     | 64.90                    | 120 (8)                  |
|       | 1.64 (s, 3 H)          | 64.88                    | 105 (5)                  |
|       | 1.33 (tt, J = 12.1, 6.1 Hz, 1H) | 42.64          | 99 (9)                  |
|       | 1.26 (s, 3H)           | 30.66                    | 95 (4)                   |
| TLC   | 26.88                  | 91 (3)                   |                          |
| Rᵣ   | 0.6                    | 24.00                    | 87 (100)                 |
| 9:1 hexanes :EtOAc | 23.55                  | 55 (4)                   |                          |

14a: Using procedure A with the following modifications gave the title compound (61.3 mg, 0.4 mmol) as a colorless liquid in a mixture of diastereomers (10:1 trans: cis) in 79% yield:

- Starting olefin 13a (77.0 mg, 0.5 mmol, 1.0 equiv.)
- 5.5 M of TBHP in decane (150 µL, 0.5 mmol, 1.5 equiv.)
- Since the product co-elutes with phenylsilane on silica, purification was achieved by flash chromatography on silica impregnated with 5% (w/w) K₂CO₃
- Column solvent: 9:1 hexanes: EtOAc

|       | ¹H NMR (400 MHz, CDCl₃) | ¹³C NMR (101 MHz, CDCl₃) | GCMS (EI, 70 eV) m/z (%) |
|-------|------------------------|--------------------------|--------------------------|
|       | 1.81-1.73 (m, 4 H)     | 73.04                    | 141 (3)                  |
|       | 1.30-1.19 (m, 3 H)     | 72.97                    | 138 (3)                  |
14b: Using procedure A with the following modifications gave the title compound (80 mg, 0.39 mmol) as a mixture of diastereomers (1 : 7.5 trans : cis) as a very pale yellow oil in 77 % yield:

- Starting olefin 14b (91.1 mg, 0.5 mmol, 1.0 equiv.)
- 8.0 M of TBHP in hexanes (93 µL, 0.5 mmol, 1.5 equiv.)
- Column Solvent: 2% EtOAc in hexanes -> 5% EtOAc in hexanes

**1H NMR (400 MHz, CDCl3)**
- 3.96-3.86 (m, 4 H)
- 1.82-1.80 (m, 2 H)
- 1.74-1.71 (m, 2 H)
- 1.57-1.43 (m, 2 H)
- 1.23 (s, 3 H)
- 1.11 (qd, J = 2.8/3.3 Hz, 2 H)
- 0.92-0.85 (m, 5 H)

**13C NMR (101 MHz, CDCl3)**
- 111.98
- 64.82
- 46.44
- 35.16
- 32.77
- 27.52
- 22.75
- 21.15

**GCMS (EI, 70 eV) m/z (%)**
- 169 (6)
- 107 (1)
- 88 (5)
- 87 (100)
- 55 (6)

**TLC**
- Rf = 0.28
- 22.68 10% EtOAc in hexanes
- 21.49 (KMnO₄)
- 17.53

**MeO**

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Me
O
O
14b
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**5% EtOAc in hexanes**

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5% EtOAc in hexanes
(dark yellow spot, p-anisaldahyde)
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**SI-1:** The title compound was prepared by a previously reported procedure. The spectral data obtained matched those previously reported.

![SI-1](image)

**15:** Using procedure A with the following modifications gave the title compound (123.5 mg, 0.71 mmol) as mixture of diastereomers (3.7:1.0 trans:cis) as a colorless oil in 71% yield:

- Starting olefin **SI-1** (172.7 mg, 1.0 mmol, 1.0 equiv.)
- Anhydrous iPrOH (2.0 mL, 0.5 M)
- Phenylsilane (732 µL, 6.0 mmol, 6.0 equiv.)
- 8.0 M of TBHP in hexanes (248 µL, 2.0 mmol, 2.0 equiv.)
- Mn(dpm)$_3$ (90 mg, 0.15 mmol, 15 mol%)
- Column solvent: hexanes

|                  | $^1$H NMR (400 MHz, CDCl$_3$) | $^{13}$C NMR (101 MHz, CDCl$_3$) | GCMS (EI, 70 eV) m/z (%) |
|------------------|-------------------------------|---------------------------------|-------------------------|
|                  | 3.79 (tt, J = 11.8, 4.3 Hz, 1 H) | 60.56                          | 176 (0.3)               |
|                  | 2.25-2.21 (m, 2 H)              | 46.87                          | 174 (1)                 |
|                  | 1.84-1.81 (m, 2 H)              | 37.89                          | 161 (0.1)               |
|                  | 1.63-1.51 (m, 2 H)              | 34.72                          | 159 (0.4)               |
|                  | 1.13-0.97 (m, 3 H)              | 27.67                          | 138 (0.1)               |
|                  | 0.84 (s, 9 H)                   | 27.63                          | 123 (20)                |
|                  |                                |                                 | 116 (2)                 |
| **TLC**          |                                |                                 |                         |
| **R$_f$**        | 0.95                           |                                 |                         |
| **hexanes**      |                                | 81 (23)                         |
| **(PMA)**        |                                | 67 (17)                         |
|                  |                                | 57 (100)                        |
|                  |                                | 56 (69)                         |

**SI-2:** The title compound was prepared by a previously reported procedure. The spectral data obtained matched those previously reported.
Using procedure A with the following modifications gave the title compound (146.8 mg, 0.67 mmol) as mixture of diastereomers (3.7:1.0 *trans:cis*) as a colorless oil in 67% yield:

- Starting olefin *SI-2* (217.2 mg, 1.0 mmol, 1.0 equiv.)
- Anhydrous iPrOH (2.0 mL, 0.5 M)
- Phenylsilane (610 µL, 5.0 mmol, 5 equiv.)
- 8.0 M of TBHP in hexanes (372 µL, 3.0 mmol, 3 equiv.)
- Mn(dpm)₃ (90 mg, 0.15 mmol, 15 mol%)
- Column solvent: hexanes

|   | ¹H NMR (400 MHz, CDCl₃) | ¹³C NMR (101 MHz, CDCl₃) | GCMS (El, 70 eV) m/z (%) |
|---|------------------------|--------------------------|--------------------------|
|   | 3.96 (ddt, *J* =11.8/8.5/4.3 Hz, 1H) | 53.05 | 220 (0.4) |
|   | 2.36-2.32 (m, 2 H) | 46.81 | 218 (0.4) |
|   | 1.81-1.72 (m, 4 H) | 38.91 | 205 (3) |
|   | 1.14-1.00 (m, 3 H) | 32.53 | 203 (3) |
|   | 0.83 (s, 9 H) | 28.87 | 163 (5) |
| TLC | | 27.63 | 161 (5) |

TLC: *R*ᵡ = 0.4 and 0.42 hexanes

4-tert-Butyl-cyclohexanone (309 mg, 2.0 mmol, 1.0 equiv.) was dissolved in DCM (10 mL) and iPr₂NEt (0.7 ml, 4.0 mmol, 2.0 equiv.) was added. The flask was cooled to 0° and TBSOTf (0.69 ml, 3.0 mmol, 1.5 equiv.) was added drop-wise via syringe. The resulting solution was stirred at 0° for 45 min, at which point the reaction was diluted with dichloromethane (10 ml) and washed with water (20 ml). The aqueous layer was then extracted with DCM (2x 15 ml) and the organic layer was dried over *Na₂SO₄*. The solvent was removed under reduced pressure and resulting clear oil was purified through a silica plug. Upon concentration, the title compound was obtained as a clear colorless oil in quantitative yield, and the spectral data collected was identical to those previously reported in literature.⁴¹
Using procedure A with the following modifications gave the title compound (211.0 mg, 0.78 mmol) as a mixture of diastereomers\(^2\) (3.9:1.0 \textit{trans:cis}) as a colorless oil in 78 \% yield:

- Starting olefin \textbf{SI-3} (268.5 mg, 1.0 mmol, 1.0 equiv.)
- Anhydrous iPrOH (2 mL, 0.5 M)
- Phenylsilane (732 µL, 6 mmol, 6 equiv.)
- 8.0 M of TBHP in hexanes (248 µL, 2.0 mmol, 2.0 equiv.)
- Mn(dpm)\(_3\) (90 mg, 0.15 mmol, 15 mol%)
- CaCO\(_3\) (20 mg, 0.2 mmol, 0.2 equiv.)
- Column solvent: hexanes

\begin{align*}
\text{H NMR (400 MHz, CDCl}\_3\text{)} & & \text{C NMR (101 MHz, CDCl}\_3\text{)} & & \text{GCMS (EI, 70 eV) m/z (\%)} \\
3.47 (tt, J = 10.8, 4.4 Hz, 1 H) & 72.28 & & 270 (0.1) \\
1.90-1.86 (m, 2 H) & 47.33 & & 269 (0.2) \\
1.75-1.72 (m, 2 H) & 36.57 & & 255 (1) \\
1.25 (q, J = 13.4 Hz, 2H) & 32.43 & & 214 (10) \\
1.05-0.93 (m, 3 H) & 27.82 & & 213 (55) \\
0.89 (s, 9 H) & 26.12 & & 197 (0.1) \\
0.84 (s, 9 H) & 25.97 & & 183 (0.1) \\
0.05 (s, 6 H) & 18.45 & & 171 (0.5) \\
& -4.40 & & 157 (0.2) \\

\text{TLC} & \text{R}_{t} = 0.85 (\text{cis}) \text{ and } 0.38 (\text{trans}) \text{ hexanes (PMA)} & & 155 (0.7) \\

\text{SI-4:} \text{ The title compound was prepared by a previously reported procedure.}^43 \text{ The spectral data obtained matched those previously reported.}^44
18: Using procedure A with the following modifications gave the title compound (35.5 mg, 0.18 mmol) as a mixture of diastereomers\(^{45}\) (6.7:1 trans:cis) as a colorless oil in 72% yield:

- Starting olefin SI-4 (48.8 mg, 0.25 mmol, 1.0 equiv.)
- Anhydrous iPrOH (0.50 mL, 0.5 M)
- Phenylsilane (186 µL, 1.5 mmol, 6.0 equiv.)
- 8.0 M of TBHP in hexanes (186 µL, 1.25 mmol, 5 equiv.)
- Mn(dpm)\(_3\) (30.0 mg, 0.05 mmol, 20 mol%)
- CaCO\(_3\) (5.0 mg, 0.05 mmol, 0.2 equiv.)
- Column solvent: 1:1 EtOAc : hexanes

|        | \(^1\)H NMR (400 MHz, CDCl\(_3\)) | \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) | GCMS (EI, 70 eV) m/z (%) |
|--------|---------------------------------|---------------------------------|------------------------|
|        | Matched those previously reported\(^{45}\) | 169.35 | 197 (5) |
|        | 48.90 | 182 (2) |
|        | 47.42 | 154 (1) |
|        | 33.77 | 140 (1) |
| TLC    | 32.46 | 126 (1) |
|        |            |            |            |
|        | 1:1 hexanes:EtOAc (faint pink-red spot, p-anisaldehyde) | 27.66 | 123 (5) |
|        | 26.22 | 98 (14) |
|        | 23.70 | 81 (13) |
|        |            | 67 (9) |
|        |            | 60 (100) |
|        |            | 57 (26) |
|        |            | 56 (23) |

Δ\(^{1,2}\)\(^{19}\): Aluminum trichloride (402 mg, 3.0 mmol, 0.1 equiv.) was added to a stirring neat solution of ethyl acrylate (3.18 mL, 30 mmol, 1.0 equiv.) and isoprene (6.0 mL, 60 mmol, 2.0 equiv.) at 0 °C. After 1 hour, the solution was diluted with DCM (20mL) and quenched with water (20mL) at 0 °C. The mixture was extracted with DCM (3 x 30 mL) and the organic phase was washed with a solution of saturated NaHCO\(_3\) (30 mL) and brine (40 mL), dried over MgSO\(_4\) and concentrated to give ethyl 2-(4-methylcyclohex-3-en-1-yl)acetate (4.87 g, 29 mmol) as a yellow oil in 97% yield.

The ester (4.87 g, 29 mmol, 1.0 equiv.) was then dissolved in ether (102 mL) and cooled to 0 °C. A 4 M LAH solution in ether (7.25 mL, 29 mmol, 1.0 equiv.) was then added drop-wise to this mixture, and after
15 minutes the reaction was allowed to warm to room temperature. After 1 hour, the reaction was quenched with sequential drop-wise additions of H$_2$O (0.1 mL), 15%(w/w) NaOH in H$_2$O (0.1 mL), and H$_2$O (0.3 mL). MgSO$_4$ was added to this stirring solution, and the resulting mixture was filtered and concentrated to yield the crude product mixture. The crude mixture was purified by column chromatography (3:1 pentane: Et$_2$O) to afford the title compound (2.64 g, 20.88 mmol) as a clear oil in 72% yield.

19: Using procedure A with the following modifications gave the title compound (52.9 mg, 0.41 mmol) as a mixture of diastereomers(5.3:1.0 trans: cis) as a clear oil in 83% yield:

- Starting olefin $\Delta^{1,2}$-19 (63.1 mg, 0.50 mmol, 1.0 equiv.)
- 5.5 M of TBHP in decane (150 µL, 0.75 mmol, 1.5 equiv.)
- Column solvent: (3:1 pentane: Et$_2$O)

|    | $^1$H NMR (500 MHz, CDCl$_3$) | $^{13}$C NMR (125 MHz, CDCl$_3$) | GCMS (EI, 70 eV) m/z (%) |
|----|------------------------------|----------------------------------|--------------------------|
| 19 | 5.34 (s, 1 H)                | 134.17                           | 126 (11)                 |
|    | 3.49 (t, $J$ = 6.4 Hz, 2 H)  | 119.93                           | 111 (0.3)                |
|    | 1.66 – 2.09 (m, 7 H)         | 67.80                            | 108 (23)                 |
|    | 1.62 (s, 3 H)                | 36.24                            | 95 (18)                  |
|    | 1.21-1.29 (m, 1 H)           | 29.57                            | 93 (100)                 |
|    | $^\text{TLC}$                | 28.42                            | 91 (27)                  |
|    | $R_f$ = 0.23                 | 25.74                            | 79 (25)                  |
|    | 3:1 hexanes:EtOAc (blue, $p$-anisaldehyde) | 23.63 | 77 (23) |

|    | GCMS (EI, 70 eV) m/z (%) |
|----|--------------------------|
|    | 67 (31)                  |

$^{1}$H NMR (500 MHz, CDCl$_3$)  | $^{13}$C NMR (125 MHz, CDCl$_3$)  | GCMS (EI, 70 eV) m/z (%) |
|-----------------|-----------------|-----------------|
| 3.41 (d, $J$ = 6.4 Hz, 2 H) | 68.81 | 126 (0.8) |
| 1.88 (s, 1 H)         | 40.35 | 110 (11) |
| 1.66 - 1.80 (m, 3 H)  | 34.80 | 97 (63)  |
| 1.34 – 1.53 (m, 2 H)  | 32.92 | 95 (46)  |
| 1.16 – 1.31 (m, 2 H)  | 29.64 | 82 (27)  |
| 0.89 – 0.98 (m, 3 H)  | 22.76 | 81 (43)  |
| 0.86 (d, $J$ = 6.6 Hz, 3 H) | 68 (19) | 68 (19) |
| $^\text{TLC}$        | 67 (18) | 55 (100) |
| $R_f$ = 0.23         |        |        |
| 3:1 hexanes:EtOAc (blue, $p$-anisaldehyde) |        |        |
Δ²⁻⁻²⁰: To a stirring solution of alcohol Δ¹⁻⁻²⁻¹⁹ (165.5 mg, 1.31 mmol, 1.0 equiv.), PPh₃ (516 mg, 1.97 mmol, 1.5 equiv.) and imidazole (133.87 mg, 1.97 mmol, 1.5 equiv.) in DCM (5.5 mL) was added I₂ (498 mg, 1.97 mmol, 1.5 equiv.) in several portions over 2 minutes and the reaction was protected from light. After 45 minutes, the reaction was quenched with a 1:4 mixture of sat. Na₂S₂O₃ and sat. NaHCO₃ (5 mL). The resulting mixture was extracted with DCM (3 × 10 mL), washed with brine (10 mL), dried over MgSO₄ and concentrated to give a crude mixture. This mixture was then re-dissolved in pentane and filtered through a plug of silica with hexanes, which upon concentration gave the title compound (280 mg, 1.20 mmol) as a clear oil in 90% yield.

| ¹H NMR (500 MHz, CDCl₃) | ¹³C NMR (125 MHz, CDCl₃) | GCMS (EI, 70 eV) m/z (%) |
|------------------------|--------------------------|-------------------------|
| 5.32 (s, 1 H)          | 134.07                   | 236 (77)                |
| 3.17 (d, J = 6.1 Hz, 2 H) | 119.67                   | 181 (0.1)               |
| 2.12 - 2.25 (m, 2 H)   | 36.11                    | 167 (2)                 |
| 1.91 - 2.06 (m, 2 H)   | 32.38                    | 155 (1)                 |
| 1.83 - 1.90 (m, 1 H)   | 29.86                    | 141 (2)                 |
| 1.67 - 1.76 (m, 2 H)   | 29.80                    | 127 (8)                 |
| 1.65 (s, 3 H)          | 23.41                    | 109 (100)               |
| 1.29 – 1.40 (m, 1 H)   | 15.13                    | 93 (19)                 |
|                         |                          | 91 (22)                 |

TLC
Rₓ = 0.78
hexanes
(iodine vapor)

20: Using procedure A with the following modifications gave the title compound (98.4 mg, 0.41 mmol) as a mixture of diastereomers (5.3:1.0 trans:cis) as a clear oil in 83% yield:

- Starting olefin Δ¹⁻⁻²⁻²⁰ (118.1 mg, 0.50 mmol, 1.0 equiv.)
- 5.5 M of TBHP in decane (150 µL, 0.75 mmol, 1.5 equiv.)
- Column solvent: hexanes

| ¹H NMR (500 MHz, CDCl₃) | ¹³C NMR (125 MHz, CDCl₃) | GCMS (EI, 70 eV) m/z (%) |
|------------------------|--------------------------|-------------------------|

SI−14
Δ\(^{12}\)-21: To a stirring solution of alcohol Δ\(^{12}\)-19 (252 mg, 2.0 mmol, 1.0 equiv.) and DMAP (1.12 g, 10 mmol, 5 equiv.) in DCM (15 mL) was added benzyl chloroformate (1.4 mL, 10 mmol, 5 equiv.). After 4 hours, the reaction was quenched with a solution of saturated NaHCO\(_3\). The resulting mixture was extracted with DCM (3 x 20 mL), washed with solutions of 1M HCl (30 mL), saturated NaHCO\(_3\) (30 mL), brine (30 mL), dried over MgSO\(_4\) and concentrated to give a crude mixture. This mixture was then purified via flash column chromatography (5% Et\(_2\)O in hexanes) to give the title compound (405 mg, 1.56 mmol) as a white solid in 78% yield.

**\(^1\)H NMR (500 MHz, CDCl\(_3\))**

- 7.32-7.40 (m, 5 H)
- 5.35 (s, 1 H)
- 5.16 (s, 1 H)
- 4.06 (m, 2 H)
- 1.68 – 2.14 (m, 6 H)
- 1.64 (s, 3 H)
- 1.29 – 1.38 (m, 1 H)

**\(^13\)C NMR (125 MHz, CDCl\(_3\))**

- 155.48
- 135.49
- 134.17
- 128.76
- 128.63
- 128.48
- 119.45
- 72.55

**GCMS (EI, 70 eV) m/z (%)**

- 198 (0.5)
- 159 (0.5)
- 125 (1)
- 108 (50)
- 107 (100)
- 93 (30)
- 91 (88)
- 79 (26)

**TLC**

- R\(_f\) = 0.32
- 1% Et\(_2\)O in hexanes
21: Using procedure A with the following modifications gave the title compound (101.9 mg, 0.39 mmol) as a mixture of diastereomers (6.2:1.0 trans:cis) as a white solid in 78% yield:

- Starting olefin Δ^{1,2}-21 (130.1 mg, 0.5 mmol, 1.0 equiv.)
- 5.5 M of TBHP in decane (150 µL, 1.0 equiv.)
- Column solvent: 1% Et₂O in hexanes

|                  | ¹H NMR (500 MHz, CDCl₃) | ¹³C NMR (125 MHz, CDCl₃) | GCMS (EI, 70 eV) m/z (%) |
|------------------|-------------------------|--------------------------|---------------------------|
|                  | 7.31 – 7.40 (m, 5H)     | 155.41                   | 262 (1)                   |
|                  | 5.16 (s, 2 H)           | 135.64                   | 152 (3)                   |
|                  | 3.97 (d, J = 6.5 Hz, 2 H) | 128.71                   | 111 (92)                  |
|                  | 0.90 – 1.81 (m, 10 H)   | 128.62                   | 95 (16)                   |
|                  | 0.88 (d, J = 6.5 Hz, 3 H) | 128.48                   | 91 (100)                  |
|                  |                         | 41.51                    | 81 (12)                   |
|                  |                         | 69.62                    | 79 (13)                   |
|                  |                         | 37.14                    | 77 (11)                   |
| TLC              |                         | 14.54                    | 69 (89)                   |
|                  | 1% Et₂O in hexanes      |                         |                           |
|                  | (UV)                    | 32.79                    | 67 (14)                   |
|                  |                         | 29.71                    | 65 (15)                   |
|                  |                         | 22.75                    | 55 (49)                   |

Δ^{1,2}-22: Iodide Δ^{1,2}-20 (255 mg, 1.1 mmol, 1.0 equiv.), K₂CO₃ (597 mg, 4.4 mmol, 4 equiv.) and phenol (0.95 mL, 1.1 mmol, 1.0 equiv.) were dissolved in DMF (4 mL) in a flask protected from light and heated at 50˚C. After 14 hours, the reaction was quenched with water (6 mL). The resulting mixture was extracted with hexanes (3 x 10 mL), washed with brine (20 mL), dried over MgSO₄ and concentrated to
give a crude mixture. This mixture was then purified via flash column chromatography (hexanes to 1% Et₂O in hexanes) to give the title compound (112 mg, 0.55 mmol) as a white solid in 51% yield.

|                      |       |                      | GCMS (EI, 70 eV) m/z (%) |
|----------------------|-------|----------------------|--------------------------|
| **1H NMR (400 MHz, CDCl₃)** |       |                      |                           |
| 7.25-7.31 (m, 2 H)     |       | 159.41               | 202 (18)                 |
| 6.88 – 6.96 (m, 3 H)   |       | 134.38               | 185 (0.1)                |
| 5.40 (s, 1 H)          |       | 129.53               | 173 (0.1)                |
| 3.84 (t, J = 5.5 Hz, 2 H) |   | 120.64               | 159 (0.2)                |
| 1.79 – 2.25 (m, 6 H)   |       | 119.82               | 145 (0.1)                |
| 1.67 (s, 3 H)          |       | 114.77               | 133 (1)                  |
| 1.38 – 1.47 (m, 1 H)   |       | 72.55                | 109 (44)                 |
|                      |       | 33.56                | 108 (82)                 |
|                      |       |                      |                           |
| **13C NMR (101 MHz, CDCl₃)** |       |                      |                           |
|                      | 159.44 |                      |                           |
|                      | 134.38 |                      |                           |
|                      | 129.53 |                      |                           |
|                      | 120.64 |                      |                           |
|                      | 119.82 |                      |                           |
|                      | 114.77 |                      |                           |
|                      | 72.55  |                      |                           |
|                      | 33.56  |                      |                           |
|                      | 159.44 |                      |                           |
|                      | 134.38 |                      |                           |
|                      | 129.53 |                      |                           |
|                      | 120.64 |                      |                           |
|                      | 119.82 |                      |                           |
|                      | 114.77 |                      |                           |
|                      | 72.55  |                      |                           |
|                      | 33.56  |                      |                           |

**TLC**
- Rₜ = 0.37
- hexanes

**GCMS**
- MeO

**22:** Using procedure A with the following modifications gave the title compound (44.7 mg, 0.22.0 mmol) as a mixture of diastereomers (5.6:1.0 trans:cis) as a white solid in 79% yield:

- Starting olefin Δ¹²-22 (54.1 mg, 0.28 mmol, 1.0 equiv.)
- Anhydrous iPrOH (0.56 mL, 0.5 M)
- Phenylsilane (34.5 µL, 0.28 mmol, 1.0 equiv.)
- 5.5 M of TBHP in decane (84 µL, 0.42 mmol, 1.5 equiv.)
- Mn(dpm)₃ (16.8 mg, 0.028 mmol, 10 mol%)  
- Column solvent: hexanes

|                      |       |                      | GCMS (EI, 70 eV) m/z (%) |
|----------------------|-------|----------------------|--------------------------|
| **1H NMR (400 MHz, CDCl₃)** |       |                      |                           |
| 7.25 – 7.33 (m, 2 H)     |       | 159.44               | 204 (16)                 |

SI-17
Δ<sup>12</sup>-<sup>23</sup>: Iodide Δ<sup>12</sup>-<sup>20</sup> (472.1 mg, 2.0 mmol, 1.0 equiv.), K<sub>2</sub>CO<sub>3</sub> (691 mg, 5 mmol, 2.5 equiv.) and 4-chloro-3-fluorophenol (293.1 mg, 2.0 mmol, 1.0 equiv.) were dissolved in DMF (10 mL) in a flask protected from light and heated at 50°C. After 14 hours, the reaction was quenched with water (6 mL). The resulting mixture was extracted with hexanes (3 x 10 mL), washed with brine (20 mL), dried over MgSO<sub>4</sub> and concentrated to give a crude mixture. This mixture was then purified via flash column chromatography (hexanes) to give the title compound (141 mg, 0.55 mmol) as a white solid in 28% yield.

|      |      |      |
|------|------|------|
| 6.88 – 6.98 (m, 3 H) | 129.60 | 159 (0.1) |
| 3.77 (d, J = 6.4 Hz, 2 H) | 120.52 | 145 (0.2) |
| 0.95 – 1.95 (m, 10 H) | 114.66 | 133 (0.4) |
| 0.92 (d, J = 6.8 Hz, 3 H) | 73.57 | 111 (6) |

**TLC**

- R<sub>f</sub> = 0.37
- hexanes (UV)

|      |      |      |
|------|------|------|
| 135.29 | 134.29 | 130.60 |
| 28.73 | 25.92 | 22.82 |

**Δ<sup>12</sup>-<sup>23</sup>:**

\[ \text{Me} \quad \Delta \quad \text{F} \quad \text{Cl} \]
Using procedure A with the following modifications gave the title compound (103.6 mg, 0.40 mmol) as a mixture of diastereomers (5.4:1.0 trans:cis) as a white solid in 81% yield:

- Starting olefin $\Delta^{1,2}$-24 (127.4 mg, 0.50 mmol, 1.0 equiv.)
- 5.5 M of TBHP in decane (150 µL, 0.75 mmol, 1.5 equiv.)
- Column solvent: hexanes

| **$^1$H NMR (500 MHz, CDCl$_3$)** | **$^{13}$C NMR (125 MHz, CDCl$_3$)** | **GCMS (EI, 70 eV) m/z (%)** |
|-----------------------------|--------------------------------------|-------------------------------|
| 7.29 – 7.35 (m, 1 H)        | 159.34                               | 258 (6)                       |
| 6.74 – 6.81 (m, 1 H)        | 130.56                               | 256 (18)                      |
| 6.68 – 6.73 (m, 1 H)        | 111.39                               | 199 (0.1)                     |
| 3.79 (d, $J = 6.4$ Hz, 2 H) | 111.37                               | 185 (0.2)                     |
| 1.0 – 2.1 (m, 10 H)         | 103.56                               | 159 (3)                       |
| 0.99 (d, $J = 6.5$ Hz, 3 H) | 103.37                               | 148 (39)                      |
|                              | 74.26                                | 146 (97)                      |
| **TLC**                     | 37.50                                | 129 (12)                      |
| $R_f = 0.48$                | 34.70                                | 117 (8)                       |
| **hexanes**                 | 32.89                                | 111 (24)                      |
| **(UV)**                    | 29.90                                | 110 (30)                      |
|                            | 29.89                                | 95 (45)                       |
|                            | 22.76                                | 82 (15)                       |
|                            |                                      | 81 (26)                       |
|                            |                                      | 69 (100)                      |
|                            |                                      | 67 (24)                       |
|                            |                                      | 55 (56)                       |
Δ^{1,2-24}: Iodide Δ^{1,2-20} (472 mg, 2.0 mmol, 1.0 equiv.), K₂CO₃ (691 mg, 5.0 mmol, 2.5 equiv.) and 4-bromophenol (346 mg, 2.0 mmol, 1.0 equiv.) were dissolved in DMF (10 mL) in a flask protected from light and heated at 50°C. After 5 hours, the reaction was quenched with water (6 mL). The resulting mixture was extracted with hexanes (3 x 10 mL), washed with brine (20 mL), dried over MgSO₄ and concentrated to give a crude mixture. This mixture was then purified via flash column chromatography (hexanes) to give the title compound (170 mg, 0.60 mmol) as a white solid in 30% yield.

| **¹H NMR (500 MHz, CDCl₃)** | **¹³C NMR (125 MHz, CDCl₃)** | **GCMS (EI, 70 eV) m/z (%)** |
|-----------------------------|-----------------------------|-----------------------------|
| 7.36 (d, J = 8.9 Hz, 2 H)   | 158.53                      | 282 (22)                    |
| 6.78 (d, J = 8.9 Hz, 2 H)   | 134.32                      | 280 (22)                    |
| 5.39 (s, 1 H)               | 132.31                      | 214 (0.1)                   |
| 3.77-3.83 (m, 2 H)          | 119.82                      | 220 (0.1)                   |
| 1.77-2.23 (m, 6 H)          | 116.45                      | 187 (0.1)                   |
| 1.67 (s, 3 H)               | 112.72                      | 185 (0.1)                   |
| 1.37 – 1.45 (m, 1 H)        | 72.83                       | 174 (19)                    |
|                             | 33.48                       | 172 (19)                    |
| **TLC**                     |                             |                             |
| Rf = 0.44                   |                             |                             |
| hexanes                     |                             |                             |
| (UV)                        |                             |                             |
|                             | 29.37                       | 157 (8)                     |
|                             | 28.59                       | 155 (8)                     |
|                             | 25.98                       | 145 (6)                     |
|                             | 23.72                       | 143 (6)                     |
|                             |                             | 131 (3)                     |
|                             |                             | 119 (2)                     |
|                             |                             | 109 (100)                   |
|                             |                             | 108 (60)                    |
|                             |                             | 93 (76)                     |
|                             |                             | 91 (20)                     |
|                             |                             | 81 (22)                     |
|                             |                             | 80 (16)                     |
|                             |                             | 79 (26)                     |
|                             |                             | 77 (20)                     |
|                             |                             | 67 (80)                     |
|                             |                             | 55(24)                      |
24: Using procedure A with the following modifications gave the title compound (112.8 mg, 0.40 mmol) as a mixture of diastereomers (5.8:1.0 trans:cis) as a white solid in 80% yield:

- Starting olefin Δ\textsuperscript{1,2}-24 (140.6 mg, 0.50 mmol, 1.0 equiv.)
- 5.5 M of TBHP in decane (150 µL, 0.75 mmol, 1.5 equiv.)
- Column solvent: hexanes

| \(^1\text{H} \text{NMR (500 MHz, CDCl}_3\)) | \(^{13}\text{C} \text{NMR (125 MHz, CDCl}_3\)) | GCMS (EI, 70 eV) m/z (%) |
|----------------------------------|-----------------------------------|--------------------------|
| 7.33 – 7.39 (m, 2 H)             | 158.56                             | 284 (12)                 |
| 6.74 – 6.80 (m, 2 H)             | 132.27                             | 282(12)                  |
| 3.72 (d, \(J = 6.4\) Hz, 1H)    | 116.42                             | 187 (1)                  |
| 1.67 – 1.91 (m, 4 H)             | 112.62                             | 185 (1)                  |
| 1.52 – 1.62 (m, 1 H)             | 73.89                              | 174 (100)                |
| 1.27-1.41 (m, 1 H)              | 37.61                              | 172 (100)                |
| 0.93 – 1.11 (m, 4 H)             | 34.74                              | 157 (5)                  |
| 0.92 (d, \(J = 6.6\) Hz, 1H)    | 32.91                              | 155 (5)                  |
|                                  | 29.95                              | 145 (4)                  |
| TLC                             | 22.82                              | 143 (4)                  |
| R\textsubscript{f} = 0.44        |                                   |                          |
| hexanes (UV)                    |                                   |                          |

\(\Delta^{1,2}\) 25: Iodide \(\Delta^{1,2}\)-20 (472 mg, 2.0 mmol, 1.0 equiv.), K\textsubscript{2}CO\textsubscript{3} (691 mg, 5.0 mmol, 2.5 equiv.) and 3-iodophenol (440 mg, 2.0 mmol, 1.0 equiv.) were dissolved in DMF (10 mL) in a flask protected from light
and heated at 50°C. After 5 hours, the reaction was quenched with water (10 mL). The resulting mixture was extracted with hexanes (3 x 20 mL), washed with brine (30 mL), dried over MgSO₄ and concentrated to give a crude mixture. This mixture was then purified via flash column chromatography (hexanes) to give the title compound (239 mg, 0.73 mmol) as a white solid in 37% yield.

| T  | H NMR (500 MHz, CDCl₃) | ¹³C NMR (125 MHz, CDCl₃) | GCMS (EI, 70 eV) m/z (%) |
|----|-----------------------|--------------------------|--------------------------|
| H  | 7.26 (broad s, 2 H)   | 159.91                   | 328 (21)                 |
| H  | 6.98 (t, J = 8.1 Hz, 1 H) | 134.10                   | 233 (0.1)               |
| H  | 6.84 – 7.02 (m, 1 H)  | 130.76                   | 220 (10)                |
| H  | 5.40 (s, 1 H)         | 129.66                   | 203 (11)                |
| H  | 3.80 (m, 2 H)         | 123.70                   | 191 (2)                 |
| H  | 1.77-2.25 (m, 6 H)    | 119.74                   | 131 (2)                 |
| H  | 1.69 (s, 3 H)         | 114.29                   | 109 (52)                |
| H  | 1.37 – 1.47 (m, 1 H)  | 94.51                    | 108 (100)               |
|    |                       | 72.66                    | 93 (71)                 |
|    |                       | 33.40                    | 91 (15)                 |
|    |                       | 29.36                    | 79 (22)                 |
|    |                       | 28.49                    | 67 (53)                 |
|    |                       | 25.90                    | 55 (16)                 |
|    |                       | 23.72                    |                         |

TLC
Rₚ = 0.51
hexanes
(UV)

GCMS (EI, 70 eV) m/z (%)

25: Using procedure A with the following modifications gave the title compound (112.8 mg, 0.40 mmol) as a mixture of diastereomers (6.6:1.0 trans:cis) as a white solid in 80% yield:

- Starting olefin Δ¹²⁻²⁴ (140.6 mg, 0.50 mmol, 1.0 equiv.)
- 5.5 M of TBHP in decane (150 µL, 0.75 mmol, 1.5 equiv.)
- Column solvent: hexanes

| T  | H NMR (500 MHz, CDCl₃) | ¹³C NMR (125 MHz, CDCl₃) | GCMS (EI, 70 eV) m/z (%) |
|----|-----------------------|--------------------------|--------------------------|
| H  | 7.25 – 7.29 (m, 2 H)  | 160.04                   | 330 (25)                 |
| H  | 6.99 (t, J = 8.0 Hz, 1 H) | 130.81                   | 233 (1)                 |
| H  | 6.84 – 6.89 (m, 1 H)  | 129.66                   | 221 (9)                 |
| H  | 3.73 (d, J = 6.4 Hz, 2 H) | 123.75                   | 220 (100)               |
| H  | 1.53 – 1.90 (m, 5 H)  | 114.36                   | 203 (8)                 |

SI-22
Δ1,2-26: Iodide Δ1,2-20 (472.18 mg, 2.0 mmol, 1.0 equiv.), K₂CO₃ (414.6 mg, 3.0 mmol, 1.5 equiv.) and 4-trifluoromethoxyphenol (356.2 mg, 2.0 mmol, 1.0 equiv.) were dissolved in DMF (8 mL) in a flask protected from light and heated at 80°C. After 5 hours, the reaction was quenched with water (10 mL). The resulting mixture was extracted with hexanes (3 x 20 mL), washed with brine (30 mL), dried over MgSO₄ and concentrated to give a crude mixture. This mixture was then purified via flash column chromatography (hexanes) to give the title compound (489 mg, 1.7 mmol) as a white solid in 85% yield.

1H NMR (500 MHz, CDCl₃) 13C NMR (125 MHz, CDCl₃) GCMS (EI, 70 eV) m/z (%)
7.13 (d, J = 9.0 Hz, 2 H) 157.95 286 (35)
6.92 – 6.82 (m, 2 H) 142.70 201 (3)
5.40 (s, 1 H) 134.28 191 (2)
3.82 (dd, J = 6.5, 3.7 Hz, 1H) 122.50 189 (2)
2.15 – 2.22 (m, 1 H) 119.82 178 (20)
2.00 – 2.10 (m, 2 H) 115.39 177 (4)
1.88 – 2.00 (m, 2 H) 99.75 161 (6)
1.70 – 1.86 (m, 1 H) 73.07 149 (3)
1.67 (s, 3 H) 33.51 109 (100)
1.37 – 1.48 (m, 1 H) 29.43 108 (54)
TLC 25.99 93 (80)
Rf = 0.51

28.57 95 (19)

GCMS (EI, 70 eV) m/z (%)
32.91 110 (31)
29.94 95 (36)
22.80 81 (18)
76 (10)
69 (64)
67 (15)
55 (38)
26: Using procedure A with the following modifications gave the title compound (116.6 mg, 0.40 mmol) as a mixture of diastereomers (5.7:1.0 trans:cis) as a white solid in 81% yield:

- Starting olefin Δ¹,²-26 (143.1 mg, 0.50 mmol, 1.0 equiv.)
- 5.5 M of TBHP in decane (150 µL, 0.75 mmol, 1.5 equiv.)
- Column solvent: hexanes

| Hexanes     | 81 (28) |
|-------------|---------|
| (UV)        | 79 (30) |
|            | 77 (22) |
|            | 69 (23) |
|            | 67 (90) |
|            | 55 (28) |

26: Using procedure A with the following modifications gave the title compound (116.6 mg, 0.40 mmol) as a mixture of diastereomers (5.7:1.0 trans:cis) as a white solid in 81% yield:

- Starting olefin Δ¹,²-26 (143.1 mg, 0.50 mmol, 1.0 equiv.)
- 5.5 M of TBHP in decane (150 µL, 0.75 mmol, 1.5 equiv.)
- Column solvent: hexanes

| Hexanes     | 81 (28) |
|-------------|---------|
| (UV)        | 79 (30) |
|            | 77 (22) |
|            | 69 (23) |
|            | 67 (90) |
|            | 55 (28) |

26: Using procedure A with the following modifications gave the title compound (116.6 mg, 0.40 mmol) as a mixture of diastereomers (5.7:1.0 trans:cis) as a white solid in 81% yield:

- Starting olefin Δ¹,²-26 (143.1 mg, 0.50 mmol, 1.0 equiv.)
- 5.5 M of TBHP in decane (150 µL, 0.75 mmol, 1.5 equiv.)
- Column solvent: hexanes

| Hexanes     | 81 (28) |
|-------------|---------|
| (UV)        | 79 (30) |
|            | 77 (22) |
|            | 69 (23) |
|            | 67 (90) |
|            | 55 (28) |

26: Using procedure A with the following modifications gave the title compound (116.6 mg, 0.40 mmol) as a mixture of diastereomers (5.7:1.0 trans:cis) as a white solid in 81% yield:

- Starting olefin Δ¹,²-26 (143.1 mg, 0.50 mmol, 1.0 equiv.)
- 5.5 M of TBHP in decane (150 µL, 0.75 mmol, 1.5 equiv.)
- Column solvent: hexanes

| Hexanes     | 81 (28) |
|-------------|---------|
| (UV)        | 79 (30) |
|            | 77 (22) |
|            | 69 (23) |
|            | 67 (90) |
|            | 55 (28) |

26: Using procedure A with the following modifications gave the title compound (116.6 mg, 0.40 mmol) as a mixture of diastereomers (5.7:1.0 trans:cis) as a white solid in 81% yield:

- Starting olefin Δ¹,²-26 (143.1 mg, 0.50 mmol, 1.0 equiv.)
- 5.5 M of TBHP in decane (150 µL, 0.75 mmol, 1.5 equiv.)
- Column solvent: hexanes

| Hexanes     | 81 (28) |
|-------------|---------|
| (UV)        | 79 (30) |
|            | 77 (22) |
|            | 69 (23) |
|            | 67 (90) |
|            | 55 (28) |

26: Using procedure A with the following modifications gave the title compound (116.6 mg, 0.40 mmol) as a mixture of diastereomers (5.7:1.0 trans:cis) as a white solid in 81% yield:

- Starting olefin Δ¹,²-26 (143.1 mg, 0.50 mmol, 1.0 equiv.)
- 5.5 M of TBHP in decane (150 µL, 0.75 mmol, 1.5 equiv.)
- Column solvent: hexanes

| Hexanes     | 81 (28) |
|-------------|---------|
| (UV)        | 79 (30) |
|            | 77 (22) |
|            | 69 (23) |
|            | 67 (90) |
|            | 55 (28) |
Δ¹²-27: Iodide Δ¹²-20 (472 mg, 2.0 mmol, 1.0 equiv.), K₂CO₃ (304 mg, 2.0 mmol, 1.0 equiv.) and 4-methoxyphenol (248 mg, 2.0 mmol, 1.0 equiv.) were dissolved in DMF (6 mL) in a flask protected from light and heated at 70°C. After 7 hours, the reaction stalled and thus extra K₂CO₃ (138 mg, 1.0 mmol, 0.5 equiv.) was added and the reaction was heated at 45 °C for an addition 24 hours. The reaction was then quenched with water (10 mL), and the resulting mixture was extracted with hexanes (3 x 20 mL), washed with brine (40 mL), dried over MgSO₄ and concentrated to give a crude mixture. This mixture was then purified via flash column chromatography (3% Et₂O in hexanes) to give the title compound (161 mg, 0.70 mmol) in 35% yield.

|        |            |            |            |
|--------|------------|------------|------------|
|        | ¹H NMR (500 MHz, CDCl₃) | ¹³C NMR (125 MHz, CDCl₃) | GCMS (EI, 70 eV) m/z (%) |
|        | 153.85     | 153.62     | 232 (27)   |
|        | 134.18     | 119.90     | 125 (9)    |
|        | 114.76     | 73.39      | 124 (100)  |
|        | 119.90     | 55.90      | 123 (6)    |
|        | 73.39      | 33.66      | 109 (32)   |
|        | 73.39      | 29.48      | 108 (11)   |
|        | 73.39      | 28.66      | 93 (17)    |
|        | 115.60     | 26.04      | 81 (8)     |
|        | 114.76     | 26.04      | 79 (8)     |
|        | 119.90     | 26.04      | 77 (9)     |
|        | 115.60     | 23.74      | 55 (7)     |

TLC

Rᵣ = 0.19

hexanes

(UV)

Δ¹²-27: Using procedure A with the following modifications gave the title compound (93.6 mg, 0.40 mmol) as a mixture of diastereomers (5.2:1.0 trans:cis) as a white solid in 80% yield:

- Starting olefin Δ¹²-27 (116.2 mg, 0.50 mmol, 1.0 equiv.)
- 5.5 M of TBHP in decane (150 µL, 0.75 mmol, 1.5 equiv.)
- Column solvent: 1% Et₂O in hexanes

|       | ¹H NMR (500 MHz, CDCl₃) | ¹³C NMR (125 MHz, CDCl₃) | GCMS (EI, 70 eV) m/z (%) |
|-------|------------------------|--------------------------|--------------------------|
|       | 6.82 – 6.85 (m, 4 H)   | 153.76                   | 234 (9)                  |
|       | 3.77 (s, 3 H)          | 153.67                   | 125 (8)                  |
|       | 3.71 (d, J = 6.4 Hz, 2 H) | 115.55                 | 124 (100)                |
|       | 1.52 – 1.92 (m, 5 H)   | 114.75                   | 123 (4)                  |
|       | 1.25 – 1.40 (m, 1 H)   | 74.44                    | 110 (2)                  |
|       | 0.92 – 1.10 (m, 4 H)   | 55.89                    | 109 (17)                 |
|       | 0.91 (d, J = 6.6 Hz, 1H) | 37.75                 | 95 (28)                  |
|       |                        |                          |                          |
|       |                        |                          |                          |
|       | ¹H NMR (500 MHz, CDCl₃) | ¹³C NMR (125 MHz, CDCl₃) | GCMS (EI, 70 eV) m/z (%) |
|       | 7.32-7.36 (m, 2 H)     | 137.47                   | 218 (24)                 |
|       | 7.25 – 7.30 (m, 2 H)   | 134.10                   | 149 (0.8)                |
|       | 7.14 – 7.18 (m, 1H)    | 128.96                   | 147 (0.8)                |
|       | 5.36 (s, 1 H)          | 128.93                   | 141 (0.7)                |
|       | 2.20-2.27 (m, 1 H)     | 125.70                   | 135 (2)                  |
|       | 1.90 – 2.00 (m, 3 H)   | 119.99                   | 124 (3)                  |
|       | 1.75 – 1.85 (m, 2 H)   | 40.06                    | 123 (17)                 |
|       | 1.65 (s, 3 H)          | 33.26                    | 110 (10)                 |
|       | 1.35 – 1.43 (m, 1 H)   | 31.58                    | 109 (19)                 |

Δ¹,₂-28: Iodide Δ¹,₂-20 (472 mg, 2.0 mmol, 1.0 equiv.), NaH (60 mg, 2.5 mmol, 1.25 equiv.) and thiophenol (220 mg, 2.0 mmol, 1.0 equiv.) were dissolved in DMF (10 mL) in a flask protected from light and heated at 50 °C. After 5 hours, the reaction was quenched with water (10 mL). The resulting mixture was extracted with hexanes (3 x 20 mL), washed with brine (40 mL), dried over MgSO₄ and concentrated to give a crude mixture. This mixture was then purified via flash column chromatography (hexanes) to give the title compound (239 mg, 0.73 mmol) in 37% yield.
28: Using procedure A with the following modifications gave the title compound (90.1 mg, 0.30 mmol) as a mixture of diastereomers (5.2:1.0 trans:cis) as a white solid in 82% yield:

- Starting olefin $\Delta^{1,2}$-28 (80.5 mg, 0.37 mmol, 1.0 equiv.)
- Anhydrous iPrOH (0.74 mL, 0.5 M)
- Phenylsilane (45 $\mu$L, 0.37 mmol, 1.0 equiv.)
- 5.5 M of TBHP in decane (111 $\mu$L, 0.56 mmol, 1.5 equiv.)
- Mn(dpm)$_3$ (22.2 mg, 0.037 mmol, 10 mol%)
- Column solvent: hexanes

| 1H NMR (500 MHz, CDCl$_3$) | 13C NMR (125 MHz, CDCl$_3$) | GCMS (EI, 70 eV) m/z (%) |
|---------------------------|-----------------------------|--------------------------|
| 7.30 – 7.35 (m, 2 H)      | 137.67                      | 220 (41)                 |
| 7.25 – 7.29 (m, 2 H)      | 128.91                      | 135 (1)                  |
| 7.13 – 7.18 (m, 1 H)      | 128.72                      | 124 (10)                 |
| 2.83 (d, $J = 6.8$ Hz, 2 H) | 125.56                      | 123 (15)                 |
| 1.22 – 1.96 (m, 6 H)      | 41.08                       | 111 (14)                 |
| 0.90 – 1.07 (m, 4 H)      | 37.51                       | 110 (100)                |
| 0.88 d, $J = 6.6$ Hz, 2 H) | 35.03                       | 109 (13)                 |

| TLC                       |                              |                          |
|---------------------------|-----------------------------|--------------------------|
| R$_f = 0.46$              |                              |                          |

hexanes

TLC $R_f = 0.46$

29.72 108 (86)
28.65 93 (100)
23.60 91 (18)
80 (18)
79 (26)
77 (20)
67 (14)
65 (10)
55 (8)
**Δ\(^{1,2}\)-29:** Alcohol Δ\(^{1,2}\)-19 (956 mg, 4.0 mmol, 1.0 equiv.), NaH (192 mg, 8.0 mmol, 2.0 equiv.) and 3-(trifluoromethyl)benzyl bromide (956 mg, 2.0 mmol, 1.0 equiv.) were dissolved in DMF (12 mL) in a flask protected from light and heated at 60°C overnight. The reaction was then cooled to room temperature and quenched with water (10 mL). The resulting mixture was extracted with hexanes (3 x 20 mL), washed with brine (40 mL), dried over MgSO\(_4\) and concentrated to give a crude mixture. This mixture was then purified via flash column chromatography (1% Et\(_2\)O in hexanes) to give the title compound (530 mg, 1.9 mmol) in 45% yield.

| **\(^1\)H NMR (500 MHz, CDCl\(_3\))** | **\(^{13}\)C NMR (125 MHz, CDCl\(_3\))** | **GCMS (EI, 70 eV) m/z (%)** |
| --- | --- | --- |
| 7.61 (broad s, 1 H) | 140.03 | 245 (0.2) |
| 7.51 – 7.56 (m, 2 H) | 134.18 | 227 (0.2) |
| 77.43 – 7.48 (m, 1 H) | 130.72 | 173 (2) |
| 4.56 (s, 2 H) | 128.92 | 160 (6) |
| 3.36 – 3.42 (m, 2 H) | 124.38 | 159 (64) |
| 2.05 – 2.15 (m, 1 H) | 124.35 | 145 (41) |
| 1.97 – 2.07 (m, 1 H) | 124.19 | 141 (7) |
| 1.82 – 1.95 (m, 3 H) | 124.16 | 127 (6) |
| 1.70 – 1.77 (m, 1 H) | 120.01 | 125 (8) |
| 1.65 (s, 3 H) | 75.86 | 119 (6) |
| 1.27 – 1.37 (m, 1 H) | 72.38 | 109 (25) |
|  & 59.37 | 108 (100) |

**TLC**  
\( R_f = 0.21 \)  
hexanes  
(\( \text{UV} \))  
26.21  
23.29  
67 (21)  
55 (15)
29: Using procedure A with the following modifications gave the title compound (106.6 mg, 0.37 mmol) as a mixture of diastereomers (6.1:1.0 trans:cis) as a white solid in 75\% yield:

- Starting olefin $\Delta^{1,2}$-28 (142.2 mg, 0.50 mmol, 1.0 equiv.)
- 5.5 M of TBHP in decane (150 $\mu$L, 0.75 mmol, 1.5 equiv.)
- Column solvent: 0.5\% Et$_2$O in hexanes

| \(^1\)H NMR (500 MHz, CDCl$_3$) | \(^{13}\)C NMR (125 MHz, CDCl$_3$) | GCMS (EI, 70 eV) m/z (%) |
|--------------------------------|----------------------------------|--------------------------|
| 7.59 (broad s, 1 H)            | 140.11                           | 267 (0.2)                |
| 7.49 – 7.55 (m, 2 H)           | 130.74                           | 176 (2)                  |
| 7.43 – 7.47 (m, 1 H)           | 128.90                           | 160 (33)                 |
| 4.54 (s, 2 H)                  | 124.36                           | 159 (100)                |
| 3.30 (d, $J = 6.4$ Hz, 1 H)    | 124.33                           | 145 (3)                  |
| 1.68-1.85 (m, 3 H)             | 124.21                           | 141 (8)                  |
| 1.45 – 1.61 (m, 2 H)           | 124.18                           | 127 (21)                 |
| 1.20 – 1.35 (m, 1 H)           | 76.89                            | 119 (6)                  |
| 0.90 – 1.02 (m, 4 H)           | 72.38                            | 110 (20)                 |
| 0.89 (d, $J = 6.5$ Hz, 2 H)    | 38.11                            | 109 (63)                 |
|                                | 35.20                            | 97 (30)                  |

TLC

$R_f = 0.21$

hexanes

(UV)

33.07 95 (16)

30.21 82 (9)

22.74 81 (23)

69 (14)

67 (12)

55 (57)
Δ^{1,2-30}: Iodide Δ^{1,2-20} (472 mg, 2.0 mmol, 1.0 equiv.), K$_2$CO$_3$ (304.0 mg, 2.0 mmol, 1.0 equiv.) and 4-imidazol-1-ylphenol (420 mg, 2.0 mmol, 1.0 equiv.) were dissolved in DMF (6.0 mL) in a flask protected from light and stirred overnight at room temperature. The reaction was then heated at 70˚C for 3 hours. Additional K$_2$CO$_3$ (100.0 mg, 0.72.0 mmol, 0.36 equiv.) was then added to the reaction and the mixture was heated at 50˚C for another 24 hours. Upon completion, the reaction was quenched with water (10 mL). The resulting mixture was extracted with hexanes (3 x 20 mL), washed with brine (40 mL), dried over MgSO$_4$ and concentrated to give a crude mixture. This mixture was then purified via flash column chromatography (3% MeOH in DCM) to give the title compound (180 mg, 0.67 mmol) as a white solid in 34% yield.

|          | $^1$H NMR (500 MHz, CDCl$_3$) | $^{13}$C NMR (125 MHz, CDCl$_3$) | LCMS (APCI)               |
|----------|-------------------------------|---------------------------------|---------------------------|
|          | 7.75 (s, 1 H)                 | 159.13                          | Calculated [M+H]$^+$: 269.2 |
|          | 7.27 – 7.30 (m, 2 H)          | 134.53                          | Found 269.2               |
|          | 7.16 – 7.32 (m, 2 H)          | 130.95                          | TLC                       |
|          | 6.95 – 7.00 (m, 2 H)          | 130.48                          | R$_f$ = 0.35              |
|          | 5.39 (s, 1 H)                 | 130.44                          | 3% MeOH in DCM            |
|          | 3.86 (dd, $J = 6.5/3.7$ Hz, 1 H) | 123.59                          | (UV)                      |
|          | 2.15 – 2.25 (m, 1 H)          | 120.06                          |                           |
|          | 1.90 – 2.10 (m, 4 H)          | 119.21                          |                           |
|          | 1.78 – 1.87 (m, 1 H)          | 115.9                           |                           |
|          | 1.67 (s, 3 H)                 | 99.99                           |                           |
|          | 1.38 – 1.46 (m, 1 H)          | 73.29                           |                           |
|          |                               | 33.75                           |                           |
|          |                               | 29.67                           |                           |
|          |                               | 28.82                           |                           |
|          |                               | 26.24                           |                           |
|          |                               | 24.00                           |                           |

30: Using procedure A with the following modifications gave the title compound (60.8 mg, 0.22 mmol) as a mixture of diastereomers (5.1:1.0 trans:cis) as a white solid in 84% yield:

- Starting olefin Δ^{1,2-30} (71.6 mg, 0.26 mmol, 1.0 equiv.)
- Anhydrous iPrOH (0.56 mL, 0.5 M)
- Phenylsilane (162.8 µL, 1.3 mmol, 5.0 equiv.)
- 5.5 M of TBHP in decane (161 µL, 0.78 mmol, 3.0 equiv.)
- Mn(dpm)$_3$ (32 mg, 0.052 mmol, 20 mol%)
- Column solvent: 3% MeOH in DCM

| $^1$H NMR (500 MHz, CDCl$_3$) | $^{13}$C NMR (125 MHz, CDCl$_3$) | LCMS (APCI) |
|-----------------------------|---------------------------------|-------------|
| 7.72 (s, 1 H)               | 158.82                          | Calculated [M+H]$^+$: 271.2 |
| 7.23-7.28 (m, 2 H)          | 130.56                          | Found 271.2 |
| 7.17 (d, $J = 9.9$ Hz, 1 H) | 130.08                          | TLC         |
| 6.93 – 6.99 (m, 2 H)        | 123.28                          | $R_f = 0.35$ |
| 3.78 (d, $J = 6.4$ Hz, 1 H) | 118.87                          | 3% MeOH in DCM (UV) |
| 1.70 – 1.93 (m, 3 H)        | 115.59                          |             |
| 1.52 – 1.63 (m, 1 H)        | 115.54                          |             |
| 1.25 – 1.40 (m, 2 H)        | 74.06                           |             |
| 0.92 – 1.13 (m, 4 H)        | 37.58                           |             |
| 0.91 (d, $J = 6.5$ Hz, 1 H) | 34.70                           |             |
|                             | 32.84                           |             |
|                             | 29.94                           |             |
|                             | 22.76                           |             |

31: Using procedure B with the following modifications gave the title compound (80.2 mg, 0.51 mmol) as a colorless oil in 82% yield:
- Starting olefin SI-4 (97.2 mg, 0.62 mmol, 1.0 equiv.)
- Anhydrous iPrOH (1.24 mL, 0.5 M)
- Phenylsilane (113 µL, 0.93 mmol, 1.5 equiv.)
- 5.5 M of TBHP in decane (372 µL, 1.86 mmol, 3 equiv.)
- Co(dpm)$_2$ (26 mg, 0.062 mmol, 10 mol%)
- Column solvent: 1% Et$_2$O in hexanes

| $^1$H NMR (400 MHz, CDCl$_3$) | $^{13}$C NMR (101 MHz, CDCl$_3$) | LCMS (APCI) |
|-----------------------------|---------------------------------|-------------|
| Matched those previously    | Matched those previously        | Calculated [M+H]$^+$: 159.1 |
| reported.$^{46}$             | reported.$^{46}$                | Found 159.1 |
|                              |                                  | TLC         |
|                              |                                  | $R_f = 0.41$ |
|                              |                                  | 5% Et$_2$O in hexanes (KMnO$_4$) |

SI-31
SI-5: A solution of acid 5-methylhex-4-enoic acid\textsuperscript{47} (216 mg, 1.7 mmol) in anhydrous DCM (4.0 mL) was treated with \textit{N},\textit{O}-dimethylhydroxylamine hydrochloride (168 mg, 1.69 mmol), WSCD·HCl (0.66 g, 3.4 mmol), and triethylamine (0.47 mL, 3.4 mmol). The reaction mixture was stirred for 15 min and quenched with a saturated solution of NaHCO\textsubscript{3}. The mixture was extracted with DCM (3 x 10 mL), washed with brine, dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, and concentrated to give a crude mixture. Purification by flash chromatography (20\% EtOAc in hexanes) gave the title compound (261.1 mg) as a colorless oil in 90\% yield.

| \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) | \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) | LCMS (APCI) |
|--------------------------------------------------------|-------------------------------------------|-------------|
| 5.13 (t, \textit{J} = 7.1 Hz, 1 H) | 174.27 | Calculated [M+H]\textsuperscript{+}: 172.1 |
| 3.67 (s, 3 H) | 132.58 | Found 172.1 |
| 3.17 (s, 3 H) | 123.07 | |
| 2.44 (t, \textit{J} = 7.5 Hz, 2 H) | 61.15 | TLC |
| 2.30 (dt, \textit{J} = 7.5, 7.1 Hz, 2 H) | 32.07 | R\textsubscript{f} = 0.21 |
| 1.68 (s, 3 H) | 25.66 | 40\% Et\textsubscript{2}O in hexanes |
| 1.62 (s, 3 H) | 23.24 | (KMnO\textsubscript{4}) |
| | 17.62 | |

32: Using procedure B with the following modifications gave the title compound (94.9 mg, 0.54 mmol) as a colorless oil in 92\% yield:

- Starting olefin SI-5 (101.8 mg, 0.59 mmol, 1.0 equiv.)
- Anhydrous iPrOH (1.18 mL, 0.5 M)
- Phenylsilane (80 \(\mu\)L, 0.59 mmol, 1.0 equiv.)
- 5.5 M of TBHP in decane (236 \(\mu\)L, 1.18 mmol, 2.0 equiv.)
- Co(dpm)\textsubscript{2} (25 mg, 0.059 mmol, 10 mol\%)
- Column solvent: 40\% Et\textsubscript{2}O in hexanes

| \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) | \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) | LCMS (APCI) |
|--------------------------------------------------------|-------------------------------------------|-------------|
| Matched those previously reported.\textsuperscript{48} | Matched those previously reported.\textsuperscript{48} | Calculated [M+H]\textsuperscript{+}: 174.1 |
| | | Found 174.1 |
| | | TLC |
| | | R\textsubscript{f} = 0.23 |
| | | 40\% Et\textsubscript{2}O in hexanes |

SI-32
SI-6: To a solution of 5-methylhex-4-enoic acid\textsuperscript{4} (0.38 g, 3.0 mmol, 1.0 equiv.), DMAP (18.1 mg, 0.148 mmol, 0.05 equiv.) and EDC (0.69 g, 3.6 mmol, 1.2 equiv.) in anhydrous DCM (5.0 mL) was added 1-dodecanethiol (0.72 ml, 3.0 mmol, 1.0 equiv.) and triethylamine (0.54 mL, 3.9 mmol, 1.3 equiv.). The reaction mixture was stirred for 1 h and quenched with sat. NaHCO\textsubscript{3}. The resulting mixture was extracted with DCM (2 x 10), washed with brine, dried over Na\textsubscript{2}SO\textsubscript{4} to yield the crude product. Purification of the crude product by flash column chromatography (0 - > 10\% Et\textsubscript{2}O in hexanes) gave the title compound (597.2 mg) as a colorless oil in 65\% yield.

- **\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3})**
  - 5.07 (t, J = 7.0 Hz, 1 H)
  - 2.84 (t, J = 7.3 Hz, 2 H)
  - 2.53 (t, J = 7.6 Hz, 2 H)
  - 2.32 (dt, J = 7.6, 7.0 Hz, 2 H)
  - 1.67 (s, 3 H)
  - 1.60 (s, 3 H)
  - 1.54 (tt, J = 7.1, 7.0 Hz, 2 H)
  - 1.40-1.16 (m, 18 H)
  - 0.87 (t, J = 6.7 Hz, 3 H)

- **\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3})**
  - 198.94
  - 133.05
  - 122.01
  - 44.04
  - 31.92
  - 29.64
  - 29.63
  - 29.61
  - 29.58
  - 29.50
  - 29.35
  - 29.14
  - 28.82
  - 28.78
  - 25.59
  - 24.29
  - 22.68
  - 17.59
  - 14.07

**LCMS**
- Calculated [M+H]\textsuperscript{+}: 313.3
- Found 313.3
- **TLC**
  - R\textsubscript{f} = 0.63
  - 5\% Et\textsubscript{2}O in hexanes

33: Using procedure A with the following modifications gave the title compound (93.5 mg, 0.29 mmol) as a colorless oil in 98\% yield:

[SI-33]
- Starting olefin **SI-6** (94.2 mg, 0.30 mmol, 1.0 equiv.)
- Anhydrous iPrOH (0.60 mL, 0.5 M)
- Phenylsilane (37 µL, 0.30 mmol, 1.0 equiv.)
- 5.5 M of TBHP in decane (49 µL, 0.6 mmol, 2.0 equiv.)
- Mn(dpm)₃ (18 mg, 0.03 mmol, 10 mol%)
- Column solvent: 1% Et₂O in hexanes

|      | ¹H NMR (400 MHz, CDCl₃) | ¹³C NMR (101 MHz, CDCl₃) | LCMS (APCI) |
|------|--------------------------|--------------------------|-------------|
|      | 2.88 (t, J = 7.3 Hz, 2 H) | 199.82                   | Calculated [M+H]+: 315.3 |
|      | 2.54 (t, J = 7.6 Hz, 2 H) | 44.36                    | Found 315.3  |
|      | 1.68 (tt, J = 7.7, 7.7 Hz, 2 H) | 38.14                    |             |
|      | 1.62-1.52 (m, 3 H) | 31.92 | |
|      | 1.41-1.18 (m, 20 H) | 29.65 | |
|      | 0.94-0.87 (m, 3 H) | 29.63 | TLC Rᵣ = 0.64 |
|      | 0.89 (d, J = 6.7, 3 H) | 29.60 | 5% Et₂O in hexanes; |
|      |                            | 29.58 | (KMnO₄) |
|      |                            | 29.49 | |
|      |                            | 29.35 | |
|      |                            | 29.13 | |
|      |                            | 28.84 | |
|      |                            | 28.82 | |
|      |                            | 27.76 | |
|      |                            | 23.63 | |
|      |                            | 22.69 | |
|      |                            | 22.44 | |
|      |                            | 14.12 | |

**SI-7**: The title compound was prepared by a previously reported procedure.⁴⁹ The spectral data obtained matched those previously reported.⁴⁹

**Me**

**SI-7**: Using procedure A with the following modifications gave the title compound (94.9 mg, 0.41 mmol) as a pale yellow oil in 69% yield:
- Starting olefin SI-7 (101.8 mg, 0.59 mmol, 1.0 equiv.)
- Anhydrous iPrOH (1.18 mL, 0.5 M)
- Phenylsilane (109 μL, 0.89 mmol, 1.5 equiv.)
- 5.5 M of TBHP in decane (178 μL, 0.89 mmol, 1.5 equiv.)
- Mn(dpm)$_3$ (35.4 mg, 0.059 mmol, 10 mol%)
- Column solvent: 100:5:1 DCM:MeOH:NH$_4$OH

$^1$H NMR (400 MHz, CD$_3$OD)  
$^{13}$C NMR (101 MHz, CD$_3$OD)  
LCMS (APCI)

Matched those previously reported.$^{50}$ Matched those previously reported.$^{50}$ Calculated [M+H]$^+$: 111.1

Found 111.1

TLC  
$R_f$ = 0.54

100:10:1 DCM:MeOH:NH$_4$OH (KMnO$_4$)

SI-8: To a solution of 6-chloropurine (0.50 g, 3.1 mmol, 1.0 equiv.) in allyl alcohol (6.2 mL, 90 mmol, 30 equiv.) was added sodium hydride (0.38 g, 9.5 mmol, 3.0 equiv.). The reaction mixture was stirred for 30 minutes then heated at 60 °C for overnight. Upon cooling, sat. aq. NH$_4$Cl (20 mL) and DCM (20 mL) were added to the reaction, and the resulting mixture was extracted with DCM (3 x 30 mL), washed with brine (100 mL), dried over Na$_2$SO$_4$ and concentrated to give the crude product. Purification of the crude material by flash column chromatography (40 ->100% EtOAc in hexanes -> 2% MeOH in EtOAc) gave the title compound (369.5 mg) as a white solid in 68% yield.

$^1$H NMR (400 MHz, d$_6$-DMSO)  
$^{13}$C NMR (101 MHz, d$_6$-DMSO)  
LCMS (APCI)

| 8.47 (s, 1 H) | 158.90 | Calculated [M+H]$^+$: 177.1 |
| 8.40 (s, 1 H) | 155.48 | Found 177.1 |
| 6.12 (ddt, J =17.2/10.5/5.4 Hz, 1H) | 151.63 | TLC |
| 5.43 (dd, J = 17.2, 1.8 Hz, 1 H) | 143.17 | $R_f$ = 0.38 |
| 5.26 (dd, J = 10.5, 1.8 Hz, 1 H) | 133.43 | 10% MeOH in EtOAc (KMnO$_4$) |
| 5.05 (d, J = 5.4 Hz, 2 H) | 118.64 |
| 67.04 | |

SI–35
35: Using procedure A with the following modifications gave the title compound (44.7 mg, 0.25 mmol) as a white solid in 56% yield:

- Starting olefin SI-8 (79.0 mg, 0.45 mmol, 1.0 equiv.)
- Anhydrous iPrOH (0.90 mL, 0.5 M)
- Phenylsilane (55 µL, 0.45 mmol, 1.0 equiv.)
- 5.5 M of TBHP in decane (135 µL, 0.68 mmol, 1.5 equiv.)
- Mn(dpm)₃ (5.4 mg, 0.009 mmol, 2 mol%)
- Column solvent: 5% MeOH in EtOAc

**1H NMR (400 MHz, d₆-DMSO)**  
Matched those previously reported.⁵⁰

**13C NMR (101 MHz, d₆-DMSO)**  
Matched those previously reported.⁵⁰

**LCMS (APCI)**  
Calculated [M+H]⁺: 179.0  
Found 179.0

**TLC**  
Rₛ = 0.40  
10% MeOH in EtOAc  
(KMnO₄)

SI-9: A solution of 4,5-dichloroimidazole (0.42 g, 3.0 mmol) in anhydrous THF (6.0 mL) was treated with sodium hydride (0.18 g, 4.5 mmol) and allyl bromide (0.29 mL, 3.4 mmol). The reaction mixture was stirred for 7 hours and quenched with a solution of saturated aq. NH₄Cl (10 mL) and diluted with ethyl acetate (10 mL). The mixture was then extracted with EtOAc (2 x 10 mL), washed with brine, dried over Na₂SO₄, and concentrated to give a crude mixture. Purification by flash chromatography (40% EtOAc in hexanes) afforded the title compound (466 mg) as colorless oil in 87% yield.

| ¹H NMR (400 MHz, CDCl₃) | ¹³C NMR (101 MHz, CDCl₃) | LCMS |
|------------------------|------------------------|------|
| 7.40 (s, 1 H)          | 134.25                 |      |
| 5.93 (ddt, J = 7.2/10.5/5.4 Hz, 1H) | 130.92                 |      |
| 5.35 (d, J = 10.3 Hz, 1 H)   | 125.78                 |      |
| 5.19 (d, J = 17.0 Hz, 1 H)   | 119.28                 |      |
| 4.53 (d, J = 5.6 Hz, 2 H)    | 113.28                 |      |

**LCMS**  
Calculated [M+H]⁺: 177.0  
Found 177.0  

**TLC**  
Rₛ = 0.43  
40% EtOAc in hexanes
36: Using procedure A with the following modifications gave the title compound (106.0 mg, 0.58 mmol) as a colorless oil in 90% yield:

- Starting olefin SI-9 (115.9 mg, 0.65 mmol, 1.0 equiv.)
- Anhydrous iPrOH (1.3 mL, 0.5 M)
- Phenylsilane (119 µL, 0.98 mmol, 1.5 equiv.)
- 5.5 M of TBHP in decane (195 µL, 0.98 mmol, 1.5 equiv.)
- Mn(dpm)$_3$ (39 mg, 0.065 mmol, 10 mol%)
- Column solvent: 15% EtOAc in hexanes

$^1$H NMR (400 MHz, CDCl$_3$) $^{13}$C NMR (101 MHz, CDCl$_3$) LCMS (APCI)
Matched those previously reported.$^{51}$ Matched those previously reported.$^{51}$

Calculated [M+H]$^+$: 179.0

TLC
$R_f$ = 0.43
40% EtOAc in hexanes
(KMnO$_4$)

35: Using procedure A with the following modifications gave the title compound (49.8 mg, 0.26 mmol) as a pale yellow oil in 50% yield:

- Starting olefin SI-8 (99.7 mg, 0.520 mmol, 1.0 equiv.)
- Anhydrous iPrOH (1.04 mL, 0.5 M)
- Phenylsilane (63 µL, 0.520 mmol, 1.0 equiv.)
- 5.5 M of TBHP in decane (156 µL, 0.78 mmol, 1.5 equiv.)
- Mn(dpm)$_3$ (31 mg, 0.0520.0 mmol, 10 mol%)
- Column solvent: 3% EtOAc in hexanes

$^1$H NMR (400 MHz, CDCl$_3$) $^{13}$C NMR (101 MHz, CDCl$_3$) LCMS (APCI)
Matched those previously reported. Matched those previously reported.

Calculated [M+H]$^+$: 195.2
SI-11: To a stirring solution of 9-decen-1-ol (1.78 mL, 10 mmol, 1.0 equiv.), PPh₃ (3.93 g, 15 mmol, 1.5 equiv.) and imidazole (1.02 mg, 15 mmol, 1.5 equiv.) in DCM (42 mL) was added I₂ (3.80 g, 15 mmol, 1.5 equiv.) in several portions over 2 minutes and the reaction was protected from light. After 2 hours, the reaction was quenched with a 1:4 mixture of sat. Na₂S₂O₃ and sat. NaHCO₃ (50 mL). The resulting mixture was extracted with DCM (3 x 50 mL), washed with brine (100 mL), dried over MgSO₄ and concentrated to give a crude mixture. This mixture was then re-dissolved in pentane and filtered through a plug of silica with hexanes, which upon concentration gave 10-iododec-1-ene (2.43 g, 9.1 mmol) as a clear oil in 91% yield.

To a stirring solution of Cs₂CO₃ (9.67 g, 27.4 mmol, 3 equiv.) in DMF (35 mL) was added thioacetic acid (1.95 mL, 27.4 mmol, 3 equiv.) drop-wise over 10 minutes. The resulting mixture was stirred for 30 minutes, and after protecting the reaction from light, 10-iododec-1-ene (2.43 g, 9.1 mmol, 1.0 equiv.) in DMF (9 mL) was added drop-wise into the reaction over 20 minutes. The resulting mixture was then heated at 45 °C for overnight and quenched with H₂O (40 mL). The resulting mixture was extracted with hexanes (3 x 50 mL), washed with brine (100 mL), dried over MgSO₄ and concentrated to give a crude mixture. This mixture was then purified via flash column chromatography (hexanes -> 1% Et₂O in hexanes) to give S-dec-9-en-1-y1 ethanethioate (1.30 g, 6.1 mmol) as a yellow oil in 67% yield.

To a stirring solution of K₂CO₃ (622 mg, 4.5 mmol, 1.5 equiv.) in MeOH (6 mL) in a flask protected from light, S-dec-9-en-1-y1 ethanethioate (643 mg, 3.0 mmol, 1.0 equiv.) in MeOH (4 mL) was added drop-wise over 5 minutes. After 30 minutes, the reaction was quenched with water (10 mL) and the mixture was extracted with hexanes (3 x 10 mL), washed with brine and concentrated to give a crude mixture. The crude mixture was then purified by column chromatography (hexanes) and concentrated to yield the title compound (337 mg, 2.0 mmol) as a clear oil in 67% yield.

| ¹H NMR (500 MHz, CDCl₃) | ¹³C NMR (125 MHz, CDCl₃) | GCMS (EI, 70 eV) m/z (%) |
|-------------------------|-------------------------|-------------------------|
| 5.76 – 5.85 (m, 1 H)    | 139.67                  | 171 (12)                |
| 4.90 – 5.04 (m, 1 H)    | 114.54                  | 157 (0.4)               |
| 2.52 (q, J = 7.4 Hz, 2 H) | 34.19                   | 143 (7)                 |
| 1.61 (p, J = 7.4 Hz, 1H) | 33.94                   | 129 (25)                |
| 1.53 (s, 4 H)           | 29.50                   | 115 (31)                |
Using procedure A with the following modifications gave a crude mixture of 1,2 didecyldisulfane:

- Starting olefin **SI-11** (71.6 mg, 0.42 mmol, 1.0 equiv.)
- Anhydrous iPrOH (0.85 mL, 0.5 M)
- Phenylsilane (51.4 µL, 2.1 mmol, 5.0 equiv.)
- 8.4 M of TBHP in hexanes (80.4 µL, 0.63 mmol, 1.5 equiv.)
- Mn(dpm)$_3$ (25.3 mg, 0.042 mmol, 10 mol%)
- Column solvent: hexanes

The crude mixture of 1,2 didecyldisulfane (118.7 mg) was dissolved in diethyl ether (15 mL). A 4M solution of LAH in diethyl ether (0.5 M, 2.0 mmol, 4.0 equiv.) was added drop-wise to this stirring solution and the reaction was stirred for 4 hours. It was then quenched with concentrated HCl (1.0 mL), diluted with water (15 mL), extracted with a 1:1 mixture of hexanes: diethyl ether (3 x 20 mL), washed with brine and concentrated. The crude product was purified via flash column chromatography (pentane) to yield the title compound (29.1 mg, 0.17 mmol) in 40% yield over 2 steps.

| H NMR (500 MHz, CDCl$_3$) | C NMR (125 MHz, CDCl$_3$) | GCMS (EI, 70 eV) m/z (%) |
|---------------------------|---------------------------|--------------------------|
| Matched those previously  | Matched those previously  | 174 (31)                 |
Using procedure A with the following modifications gave the title compound in 56% GC yield (with dichlorobenzene as internal standard, calibrated against a 2.2:1.0 mixture of dichlorobenzene:decanal):

- Starting olefin 9-decenal (77.1 mg, 0.5 mmol, 1.0 equiv.)
- 8.0 M of TBHP in hexanes (37.5 µL, 0.75 mmol, 1.5 equiv.)
- Dichlorobenzene (56 µL, 0.5 mmol, 1.0 equiv.)

Cp₂ZrCl₂ (4.22 g, 14.4 mmol) was dissolved in anhydrous DCM (90 mL) in a 3-neck flask and was cooled to –30 °C. To this solution, a 2.0 M solution of AlMe₃ in hexanes (36 mL, 72.0 mmol) was added drop-wise over 10 min. After the reaction was stirred for 10 min at –30 °C, water (0.65 mL, 36 mmol) was added.
added very slowly reaction. A solution of (but-3-yn-1-yloxy)(tert-butyl)diphenylsilane (11.1 g, 36.1 mmol) in anhydrous DCM (10 mL) was added drop-wise into the mixture. The reaction was then warmed up to room temperature and stirred for another 50 minutes. Gaseous formaldehyde, formed by cracking paraformaldehyde (6.51 g, 217 mmol) at 150 °C, was then bubbled through the solution over 30 minutes. The reaction was then quenched with 3M HCl (50 mL) and diluted with DCM (50 mL) and the mixture was extracted with DCM (3 x 50 mL), washed with brine, dried over Na$_2$SO$_4$ and concentrated to yield the crude product mixture. The crude material was then purified via column chromatography (10% -> 40% EtOAc in hexanes) to yield the title compound (7.44 g) as a colorless oil in 58% yield.

$^1$H NMR (400 MHz, CDCl$_3$)  
7.69 (d, $J = 7.2$, 4 H)  
7.42 (m, 6 H)  
5.43 (t, $J = 7.1$, 1 H)  
4.15 (d, $J = 7.1$, 2 H)  
3.77 (l, $J = 6.6$, 2 H)  
2.29 (l, $J = 6.6$, 2 H)  
1.64 (s, 3 H)  
1.07 (s, 9 H)  

$^{13}$C NMR (101 MHz, CDCl$_3$)  
136.48  
135.65  
133.96  
129.68  
127.71  
125.62  
62.76  
59.24  
42.62  
26.96  
19.29  
16.59  

LCMS  
Calculated [M+H]$^+$: 337.2  
Found 337.2

TLC  
$R_f = 0.68$

40% EtOAc in hexanes  
($\rho$-anisaldehyde)

40: Using procedure A with the following modifications gave the title compound (92.9 mg, 0.26 mmol) as a colorless oil in 72% yield:

- **Starting olefin SI-12** (127.8 mg, 0.36 mmol, 1.0 equiv.)
- Anhydrous iPrOH (0.72 mL, 0.5 M)
- Phenylsilane (132 µL, 1.08 mmol, 3 equiv.)
- 5.5 M of TBHP in decane (108 µL, 0.5 mmol, 1.5 equiv.)
- Mn(dpm)$_3$ (21.6 mg, 0.036 mmol, 10 mol%)
- Column solvent: 5% EtOAc in hexanes

$^1$H NMR (400 MHz, CDCl$_3$)  
Matched those previously reported.$^{54}$

$^{13}$C NMR (101 MHz, CDCl$_3$)  
Matched those previously reported.$^{54}$

LCMS (APCI)  
Calculated [M+H]$^+$: 357.2  
Found 357.2
The title compound was prepared by a previously reported procedure.\textsuperscript{55} The spectral data obtained matched those previously reported.\textsuperscript{55}

\textbf{42b:} Using procedure A with the following modifications gave the title compound as a mixture of diastereomers (10.5:1.0 \textit{trans}:\textit{cis}) in 66\% GC yield (with dichlorobenzene as internal standard, calibrated against a 1:1 mixture of decalin and dichlorobenzene):

- Starting olefin \textbf{41} (27.3 mg, 0.2 mmol, 1.0 equiv.)
- Anhydrous iPrOH (0.4 mL, 0.5 M)
- Phenylsilane (24.4 µL, 0.2 mmol, 1.0 equiv.)
- 8.4 M of TBHP in hexanes (35.8 µL, 0.3 mmol, 1.5 equiv.)
- Mn(dpm)\textsubscript{3} (12 mg, 0.02 mmol, 10 mol%)  
- Dichlorobenzene (22.4 µL, 0.2 mmol, 1.0 equiv.)

\textbf{GCMS (EI, 70 eV) m/z (\%)}

| m/z | Percentage |
|-----|------------|
| 138 | (100)      |
| 118 | (7)        |
| 109 | (17)       |
| 96  | (62)       |
| 95  | (62)       |
| 82  | (64)       |
| 81  | (59)       |
| 79  | (20)       |
| 69  | (34)       |
| 68  | (76)       |
| 67  | (96)       |
| 59  | (28)       |
43: The title compound was prepared by a previously reported procedure\textsuperscript{35}. The spectral data obtained matched those previously reported\textsuperscript{35}.

44b: Using procedure A with the following modifications gave the title compound as a mixture of diastereomers (2.0:1.0 trans:cis) in 69% GC yield (with dichlorobenzene as internal standard, calibrated against a 1:1 mixture of dichlorobenzene and dimethylcyclohexane):

- Starting olefin 43 (55.1 mg, 0.5 mmol, 1.0 equiv.)
- 8.4 M of TBHP in hexanes (92 µL, 0.75 mmol, 1.5 equiv.)
- Dichlorobenzene (56 µL, 0.5 mmol, 1.0 equiv.)

\begin{center}
\begin{tabular}{c|c}
\textbf{GCMS (EI, 70 eV) m/z (\%)} & \\
112 (29) & \\
97 (100) & \\
84 (7) & \\
83 (14) & \\
70 (20) & \\
69 (24) & \\
68 (10) & \\
67 (9) & \\
56 (22) & \\
55 (69) & \\
\end{tabular}
\end{center}

45: The title compound was prepared by a previously reported procedure\textsuperscript{55}. The spectral data obtained matched those previously reported\textsuperscript{55}.
46b: Using procedure A with the following modifications gave the title compound (48.9 mg, 0.26 mmol) as mixture a diastereomers (3.9:1.0 trans:cis) as a colorless oil in 69% yield:

- Starting olefin 45 (70.7 mg, 0.37 mmol, 1.0 equiv.)
- Anhydrous iPrOH (0.74 mL, 0.5 M)
- Phenylsilane (45.1 µL, 0.37 mmol, 1.0 equiv.)
- 5.5 M of TBHP in decane (111 µL, 0.56 mmol, 1.5 equiv.)
- Mn(dpm)₃ (22.2 mg, 0.036 mmol, 10 mol%)
- Column solvent: 2% EtOAc in hexanes

| ¹H NMR (400 MHz, CDCl₃) | ¹³C NMR (101 MHz, CDCl₃) | LCMS (APCI) |
|-------------------------|-------------------------|-------------|
| Matched those previously reported.⁵⁵ | Matched those previously reported.⁵⁵ | Calculated [M+H]⁺: 195.2 |
|                          |                         | Found 195.2 |
|                          |                         | TLC |
|                          |                         | Rₜ = 0.55 |
|                          |                         | 10% EtOAc in hexanes |

(p-anisaldehyde)

47: (−)-Drimenol (100.2 mg, 0.45 mmol, 1.0 equiv., prepared by the reported conditions²⁹) was dissolved in anhydrous DCM (2.0 mL) and cooled to 0 °C. To this stirring mixture was added TMEDA (0.61 mL, 4.1 mmol, 9.0 equiv.) and MsCl (0.21 mL, 2.7 mmol, 6.0 equiv.). After 5 minutes, still at 0 °C, the reaction was quenched with a solution of saturated NaHCO₃ (10 mL). The resulting mixture was then extracted with DCM (2 x 10 mL), washed with brine (10 mL), dried over Na₂SO₄, and concentrated to give a pale yellow oil, which was used for the next step without further purification.

LAH (85.5 mg, 2.25 mmol) was added to a stirring solution of the crude oil in THF (3.0 mL), and the resultant mixture was heated at 50 °C for 3 hours. Upon cooling to room temperature, the reaction mixture was diluted with Et₂O (5 mL), and H₂O (90 µL), aq NaOH (90 µL, 15% w/v), and H₂O (0.27 mL) was added sequentially to the stirring solution. The mixture was then filtered and concentrated to give a
crude oil. This crude product was then purified by flash column chromatography (hexanes) to afford the title compound (67.2 mg) as a colorless oil in 72% yield over 2 steps.

|        |        | GCMS (EI, 70 eV) m/z (%) |        |
|--------|--------|--------------------------|--------|
|        |        | Matched those previously reported. |        |
|        |        | **TLC**                  |        |
|        |        | Rf = 0.90                |        |
|        |        | hexanes                  |        |
|        |        | (iodine vapor)           |        |

|                         | 1H NMR (400 MHz, CDCl₃) | 13C NMR (101 MHz, CDCl₃) |
|-------------------------|-------------------------|--------------------------|
| 5.47-5.40 (m, 1 H)      | 135.47                  | Matched those previously reported. |
| 2.06-1.95 (m, 1 H)      | 121.49                  | Matched those previously reported. |
| 1.94-1.80 (m, 1 H)      | 50.16                   | Matched those previously reported. |
| 1.63 (s, 3 H)           | 48.75                   | Matched those previously reported. |
| 1.61-1.51 (m, 1 H)      | 42.32                   | Matched those previously reported. |
| 1.51-1.40 (m, 1 H)      | 39.61                   | Matched those previously reported. |
| 1.26-1.17 (m, 2 H)      | 35.76                   | Matched those previously reported. |
| 1.03-0.94 (m, 1 H)      | 33.32                   | Matched those previously reported. |
| 0.93 (s, 3 H)           | 32.95                   | Matched those previously reported. |
| 0.91-0.86 (m, 3 H)      | 23.77                   | Matched those previously reported. |
| 0.90 (s, 3 H)           | 21.99                   | Matched those previously reported. |
| 0.77 (s, 3 H)           | 21.77                   | Matched those previously reported. |
|                         | 18.97                   | Matched those previously reported. |
|                         | 13.25                   | Matched those previously reported. |
|                         | 11.42                   | Matched those previously reported. |

**48b**: Using procedure B with the following modifications gave the title compound (37.2 mg, 0.18 mmol) as a mixture of diastereomers (6:0:1.0 trans:cis) as a clear oil in 77% yield:

- Starting olefin 47 (47.9 mg, 0.23 mmol, 1.0 equiv.)
- Anhydrous α, α, α–trifluorotoluene (2.3 mL, 0.1 M)
- Phenylsilane (42.7 µL, 1.5 equiv.)
- 8.4 M of TBHP in hexanes (166 µL, 6.0 equiv.)
- Co(dpm)$_2$ (9.8 mg, 10 mol%)
- Column solvent: pentane

|        |        | GCMS (EI, 70 eV) m/z (%) |        |
|--------|--------|--------------------------|--------|
|        |        | Matched those previously reported. |        |
|        |        | **TLC**                  |        |

|        | 1H NMR (400 MHz, CDCl₃) | 13C NMR (101 MHz, CDCl₃) | GCMS (EI, 70 eV) m/z (%) |
|--------|-------------------------|--------------------------|--------------------------|
|        | Matched those previously reported. | Matched those previously reported. | 208 (19) |
|        | Matched those previously reported. | Matched those previously reported. | 193 (30) |
|        | Matched those previously reported. | Matched those previously reported. | 138 (5) |
|        | Matched those previously reported. | Matched those previously reported. | 137 (9) |
49: To a flask charged with NaH (1.0 g, 25 mmol, 2.5 equiv.) in THF (43 mL) at 0 °C was added drop-wise a solution of dimethyl malonate (1.52 mL, 10 mmol, 1.0 equiv.) in THF (10 mL). The resulting solution was stirred for 15 minutes at 0 °C and warmed to room temperature. 3-Methyl-2-bromopropene (2 mL, 20 mmol, 2.0 equiv.) was then added drop-wise into the reaction and a condenser was fitted to the flask. The resulting mixture was heated at reflux for 24 hours. After the mixture was cooled back to room temperature, it was quenched with NH₄Cl and extracted with diethyl ether (3 x 75 mL), washed with brine (100 mL), dried over MgSO₄ and concentrated to yield a crude oil. The crude mixture was then purified by flash column chromatography (10% Et₂O in hexanes) to yield the title compound (320 mg, 1.20 mmol) as a yellow oil in 12% yield.

| Rf = 0.95 | GCMS (EI, 70 eV) m/z (%) |
|------------|-------------------------|
| 124 (16)   | 123 (100)               |
| 122 (11)   | 108 (24)                |
| 97 (10)    | 96 (13)                 |
| 93 (39)    | 82 (15)                 |
| 81 (26)    | 69 (27)                 |
| 67 (18)    | 65 (24)                 |

**1H NMR (600 MHz, CDCl₃)**

- 4.84 (s, 2 H)
- 4.73 (s, 2 H)
- 4.16 (q, J = 7.1 Hz, 1 H)
- 2.74 (s, 4 H)
- 1.68 (s, 6 H)
- 1.24 (t, J = 7.1 Hz, 6H)

**13C NMR (151 MHz, CDCl₃)**

- 173.33
- 61.63
- 57.16
- 47.39
- 43.87
- 24.27
- 14.18

**TLC**

- Rf = 0.24
- 10% hexanes in Et₂O (iodine vapor)

- 149 (7)
- 139 (4)
- 125 (5)
- 122 (11)
Using procedure A with the following modifications gave the title compound (46.1 mg, 0.17 mmol) as a mixture of isomers 50 and 51 (2.4:1.0 50:51) as a colorless oil in 85% yield, which was enriched by chromatography to (4.4:1.0 50:51) in 49% yield:

- Starting diene 49 (53.67 mg, 0.20 mmol, 1.0 equiv.)
- Anhydrous iPrOH (1 mL, 0.20 M)
- Phenylsilane (24.4 µL, 0.20 mmol, 1.0 equiv.)
- 8.0 M of TBHP in hexanes (37.5 µL, 0.30 mmol, 1.5 equiv.)
- Mn(dpm)$_3$ (12.0 mg, 0.02 mmol, 10 mol%)
- Column solvent: 1% Et$_2$O in hexanes

| $^1$H NMR (600 MHz, CDCl$_3$) | $^{13}$C NMR (151 MHz, CDCl$_3$) | GCMS (EI, 70 eV) m/z (%) |
|-----------------------------|---------------------------------|--------------------------|
| 4.16 (q, $J = 7.1$ Hz, 4 H) | 173.33                          | 270 (0.4)                |
| 2.29 (s, 4 H)               | 77.16                           | 255 (1)                  |
| 1.22 (t, $J = 7.1$ Hz, 2 H) | 61.63                           | 225 (9)                  |
| 0.87 (s, 12 H)              | 57.16                           | 214 (34)                 |
|                             | 47.39                           | 197 (29)                 |
|                             | 43.87                           | 196 (13)                 |
|                             | 24.27                           | 186 (2)                  |
|                             | 14.18                           | 181 (17)                 |
|                             |                                 | 173 (40)                 |
|                             |                                 | 168 (11)                 |
|                             |                                 | 151 (11)                 |
|                             |                                 | 142 (5)                  |
|                             |                                 | 127 (9)                  |
|                             |                                 | 123 (52)                 |
|                             |                                 | 122 (100)                |
|                             |                                 | 109 (12)                 |
4. Relative Reactivity Studies

The relative reactivity of variously substituted alkenes was qualitatively estimated by determining the amount of each starting material at the end of a reaction relative to its initial amount. This difference was quantified with quantitative $^{13}$C NMR on a Bruker DRX 600 with a Cryoprobe tuned to $^{13}$C nuclei. Values for the amounts of each substrate came from integration of the sp$^2$ (or sp in the case of the alkyne) carbons for each substrate. Roughly 8 mg. of Cr(acac)$_3$ was added to each NMR sample to facilitate $^{13}$C nuclei relaxation, and a 5xT1 value of 5.76 seconds was used based on evaluation of the T1 relaxation time of dec-1-ene. (A D7 value = 0.8 sec. was found, and D1 = D7x1.44*5 = 5.76 sec.) All substrates were found to have nuclei that relaxed within that time period when Cr$^{III}$(acac)$_3$ was used as a T1 relaxation agent. NMR experiments were run until the signal to noise ratio of the representative $^{13}$C nuclei of the least abundant substrate in an experiment was $\geq 60$.

Starred* substrates in the experiments below were excluded from the conclusions because their initial concentration were less than $\sim$1:1 with the other starting materials.

Experiments:

To a 10 mL round bottom flask was added (E)-ethyl undec-2-enoate (63.7 mg, 0.3 mmol, 1.5 equiv.), a 1.00:0.54 mix of E:Z-1-methoxydec-1-ene (51.1 mg, 0.3 mmol, 1.5 equiv.), 2,3-dimethylundec-2-ene (58.9 mg, 0.3 mmol, 1.5 equiv.), 2-methylundec-2-ene (50.5 mg, 0.3 mmol, 1.5 equiv.), dec-1-yne (41.5 mg, 0.3 mmol, 1.5 equiv.) and iPrOH (0.6 mL) under an Argon atmosphere. The mixture was stirred vigorously, then 1/3 of the mixture was removed, concentrated, and placed into an NMR tube for the initial starting material ratio (see below). To the remaining material was added phenylsilane (24.6 µL, 21.6 mg, 0.20 mmol, 1.0 equiv.) and tert-butylhydroperoxide (50.0 µL of 6.0 M in DCM; 0.3 mmol, 1.5 equiv.), and
the solution was degassed for 10 minutes. Mn(dpm)$_3$ (12.1 mg, 0.02 mmol, 0.1 equiv.) was added and the solution was degassed another 30 seconds. The reaction was then stirred at 500 rpm for 1.0 hours, at which point the reaction was quenched by the addition of NH$_4$OH (1:1 v/v aq., 2.0 mL). The reaction was extracted with hexanes (3x 5 mL), and the combined organic layer was dried over MgSO$_4$, filtered and concentrated carefully *in vacuo* to minimize loss of starting material. The resulting brown oil was flushed through a plug of silica (~5 mL) with 100% hexanes and the solution was carefully concentrated to obtain a yellow oil. The resulting oil was placed in an NMR tube. Cr(acac)$_3$ (~8 mg.) was added to both tubes, dissolved, and spectra were obtained on the DRX 600 equipped with a Cryoprobe.

**Initial NMR data:**

|       | $\text{C}_9\text{H}_{17}$ | $\text{C}_9\text{H}_{19}$ | $\text{C}_8\text{H}_{17}$ | $\text{C}_8\text{H}_{17}$ | $\text{C}_8\text{H}_{17}$ | $\text{C}_8\text{H}_{17}$ |
|-------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| $^{13}$C NMR peaks (ppm) | 124.85 | 123.40 | 68.00 | 103.18 | 107.11 | 121.04 |
| Relative Area | 0.93 | 1.00 | 0.80 | 0.64 | 0.35 | 0.98 |
| Average Area | 0.93 | 1.01 | 0.79 | 0.65 | 0.37 | 0.98 |
| Normalized area | 0.92 | 1.00 | 0.78 | 0.64 | 0.37 | 0.97 |

**Post reaction NMR data:**

|       | $\text{C}_9\text{H}_{17}$ | $\text{C}_9\text{H}_{19}$ | $\text{C}_8\text{H}_{17}$ | $\text{C}_8\text{H}_{17}$ | $\text{C}_8\text{H}_{17}$ | $\text{C}_8\text{H}_{17}$ |
|-------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| $^{13}$C NMR peaks (ppm) | 124.83 | 123.30 | 67.90 | 102.84 | 107.01 | 121.04 |
| Relative Area | 0.78 | 0.96 | 0.40 | 0.59 | 0.24 | 0.18 |
| Average Area | 0.77 | 1.04 | 0.40 | 0.60 | 0.24 | 0.18 |
| Rel. % of alkene(yne) remaining | 84 | 100 | 51* | 94* | 65* | 20 |
To an oven dried 5 mL round bottom flask was added a stir bar, dec-1-ene (32.6 mg, 0.232.0 mmol, 1.5 equiv.), 2-methylundec-1-ene (39.1 mg, 0.232.0 mmol, 1.5 equiv.) and E-ethyl undec-2-enoate (49.3 mg, 0.232.0 mmol, 1.5 equiv.) under an argon atmosphere. The mixture was stirred vigorously, then ~1/5 of the mixture was removed and placed into an NMR tube for the initial starting material ratio (see below). To the remaining material was added isopropanol (0.46 mL), phenylsilane (19.1 µL, 0.155 mmol, 1.0 equiv.) and tert-butylhydroperoxide (38.7 µL of 6.0 M in DCM; 0.232.0 mmol, 1.5 equiv.), and the solution was degassed for 10 minutes. Mn(dpim)₃ (9.4 mg, 0.015 mmol, 0.015 equiv.) was added and the solution was degassed another 30 seconds. The reaction was then stirred at 500 rpm for 1.0 hours, at which point the reaction was quenched by the addition of NH₄OH (1:1 v/v aq., 1.5 mL). The reaction was extracted with hexanes (3x 5 mL) and the combined organic layer was dried over MgSO₄, filtered and concentrated carefully in vacuo to minimize loss of starting material. The resulting brown oil was flushed through a plug of silica (~5 mL) with 5% ethyl acetate in hexanes and the solution was carefully concentrated to obtain a yellow oil. The resulting oil was placed in an NMR tube. Cr(acac)₃ (~8 mg.) was added to both tubes, dissolved, and spectra were obtained on the DRX 600 equipped with a Cryoprobe.

**Initial NMR data:**

|               | C₆H₁₇ | C₆H₁₉ | C₆H₁₇ CO₂Et |
|---------------|-------|-------|-------------|
| ¹³C NMR peaks (ppm) |       |       |             |
|                | 113.99 | 109.41 | 121.11      |
|                | 139.16 | 146.23 | 149.40      |
| Relative Area  | 0.94  | 0.95  | 1.01        |
|                | 0.97  | 0.94  | 0.98        |
| Average Area   | 0.96  | 0.95  | 1.01        |
| Normalized area| 0.95  | 0.94  | 1.00        |

**Post reaction NMR data:**

|               | C₆H₁₇ | C₆H₁₉ | C₆H₁₇ CO₂Et |
|---------------|-------|-------|-------------|
| ¹³C NMR peaks (ppm) |       |       |             |
|                | 113.84 | 109.36 | 121.10      |
|                | 138.85 | 146.76 | 149.04      |
| Relative Area  | 0.87  | 1.00  | 1.31        |
|                | 0.85  | 0.97  | 1.30        |
| Average Area   | 0.86  | 0.99  | 1.31        |
| Normalized Area| 0.66  | 0.76  | 1.00        |
| Rel. % of alk-ene remaining | 69 | 81 | 100 |
To an oven dried 5 mL round bottom flask was added a stir bar and a ~1:1 mixture of Z:E-undec-2-ene (25.5 mg, 0.165 mmol, 2.0 equiv.; see below for $^{13}$C NMR of starting material) under an Argon atmosphere. To this was added isopropanol (0.33 mL), phenylsilane (10.2 µL., 8.9 mg, 0.0825 mmol, 1.0 equiv.), and tert-butylhydroperoxide (20.6 µL of 6.0 M in DCM; 0.12 mmol, 1.5 equiv.) and the solution was degassed for 10 minutes. Mn(dpm)$_3$ (5.0 mg, 8.26 µmol, 0.10 equiv.) was added and the solution was degassed another 30 seconds. The reaction was then stirred at 500 rpm for 30 minutes, at which point the reaction was quenched by the addition of NH$_4$OH (1:1 v/v aq., 0.5 mL). The reaction was extracted with hexanes (2x 5 mL), and the combined organic layer was dried over MgSO$_4$, filtered and concentrated carefully in vacuo to minimize loss of starting material. The resulting brown oil was flushed through a plug of silica (~5 mL) with hexanes (100%) and the solution was carefully concentrated to obtain a clear colorless oil. The resulting oil was placed in an NMR tube. Cr(acac)$_3$ (~8 mg.) was added to the tube, dissolved, and a spectrum was obtained on the DRX 600 equipped with a Cryoprobe.

**Initial NMR data:**

| $^{13}$C NMR peaks (ppm) | C$_{6}$$^{13}$H$_{17}$ | C$_{6}$$^{13}$H$_{17}$ |
|--------------------------|-----------------|-----------------|
| 124.34                   | 131.53          |
| 123.42                   | 130.74          |
| Relative Area            | 1.05            | 1.13            |
|                          | 1.00            | 1.10            |
| Average Area              | 1.03            | 1.12            |
| Normalized area           | 1.00            | 1.09            |

**Post reaction NMR data:**

| $^{13}$C NMR peaks (ppm) | C$_{6}$$^{13}$H$_{17}$ | C$_{6}$$^{13}$H$_{17}$ |
|--------------------------|-----------------|-----------------|
| 124.34                   | 131.54          |
| 123.42                   | 130.75          |
| Relative Area            | 1.01            | 0.53            |
|                          | 1.00            | 0.55            |
| Average Area              | 1.01            | 0.54            |
| Rel. % of alk-ene remaining | 101          | 50              |
To an oven dried 5 mL round bottom flask was added a stir bar, dec-1-ene (27.3 mg, 0.194 mmol, 1.5 equiv.), 2-methylundec-1-ene (32.7 mg, 0.194 mmol, 1.5 equiv.), a 1:1 mixture of Z:E-undec-2-ene (60.0 mg, 0.389 mmol, 3.0 equiv.), and 2-methylundec-2-ene (32.7 mg, 0.194 mmol, 1.5 equiv.) under an Argon atmosphere. The mixture was stirred vigorously, then 1/3 of the mixture was removed and placed into an NMR tube for the initial starting material ratio (see below). To the remaining material was added isopropanol (0.26 mL), phenylsilane (16 µL, 14.1 mg, 0.3 mmol, 1.0 equiv.), and tert-butylhydroperoxide (35.3 µL of 5.5 M in DCM; 0.194 mmol, 1.5 equiv.), and the solution was degassed for 10 minutes. Mn(dpm)$_3$ (7.9 mg, 0.0130 mmol, 0.10 equiv.) was added and the solution was degassed another 30 seconds. The reaction was then stirred at 500 rpm for 1.0 hours, at which point the reaction was quenched by the addition of NH$_4$OH (1:1 v/v aq., 1.0 mL). The reaction was extracted with hexanes (3x 5 mL), and the combined organic layer was dried over MgSO$_4$, filtered and concentrated carefully \textit{in vacuo} to minimize loss of starting material. The resulting brown oil was flushed through a plug of silica (~5 mL) with hexanes (100%) and the solution was carefully concentrated to obtain a clear colorless oil. The resulting oil was placed in an NMR tube. Cr(acac)$_3$ (~8 mg.) was added to both tubes, dissolved, and spectra were obtained on the DRX 600 equipped with a Cryoprobe.

**Initial NMR data:**

|                  | $\text{C}_8\text{H}_{17}$ | $\text{C}_9\text{H}_{19}$ | $\text{C}_{10}\text{H}_{17}$ | $\text{C}_{11}\text{H}_{17}$ | $\text{C}_{12}\text{H}_{17}$ |
|------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| $^{13}$C NMR peaks (ppm) | 113.99                    | 109.42                    | 124.41                    | 123.48                    | 124.88                    |
| Relative Area    | 1.24                      | 1.02                      | 1.26                      | 1.20                      | 1.20                      |
| Average Area     | 1.22                      | 1.00                      | 1.26                      | 1.22                      | 1.19                      |
| Normalized area  | 1.03                      | 0.85                      | 1.06                      | 1.03                      | 1.00                      |

**Post reaction NMR data:**

|                  | $\text{C}_8\text{H}_{17}$ | $\text{C}_9\text{H}_{19}$ | $\text{C}_{10}\text{H}_{17}$ | $\text{C}_{11}\text{H}_{17}$ | $\text{C}_{12}\text{H}_{17}$ |
|------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| $^{13}$C NMR peaks (ppm) | 113.99                    | 109.43                    | 124.40                    | 123.47                    | 124.89                    |
| Relative Area    | 0.86                      | 1.03                      | 1.85                      | 1.39                      | 1.93                      |
| Average Area     | 0.86                      | 1.01                      | 1.88                      | 1.44                      | 1.88                      |
| Normalized Area  | 0.46                      | 0.54                      | 1.00                      | 0.77                      | 1.00                      |
| Rel. % of alk-ene remaining | 45                      | 64                        | 94                        | 75                        | 100                       |
To an oven dried 10 mL round bottom flask was added a stir bar, dec-1-ene (42.1 mg, 0.3 mmol, 1.5 equiv.), 2,3-dimethyldec-2-ene (58.9 mg, 0.3 mmol, 1.5 equiv.) and 1,2-dichlorobenzene (44.1 mg, 0.3 mmol, 1.5 equiv.) under an argon atmosphere. The mixture was stirred vigorously, then 1/3 of the mixture was removed and placed into an NMR tube for the initial starting material ratio (see below). To the remaining material was added isopropanol (0.6 mL), phenylsilane (37.0 µL., 32.5 mg, 0.3 mmol, 1.5 equiv.), and tert-butylhydroperoxide (81.8 µL of 5.5 M in nonane; 44.1 mg, 0.45 mmol, 2.25 equiv.), and the solution was degassed for 10 minutes. Mn(dpm)$_3$ (9.1 mg, 0.015 mmol, 0.075 equiv.) was added and the solution was degassed another 30 seconds. The reaction was then stirred at 500 rpm for 30 minutes, at which point the reaction was quenched by the addition of NH$_4$OH (1:1 v/v aq., 1.0 mL). The reaction was extracted with hexanes (2x 5 mL) and the combined organic layer was dried over MgSO$_4$, filtered and concentrated carefully in vacuo to minimize loss of starting material. The resulting brown oil was flushed through a plug of silica (~5 mL) with pentanes (100%) and the solution was carefully concentrated to obtain a clear colorless oil. The resulting oil was placed in an NMR tube. Cr(acac)$_3$ (~8 mg.) was added to both tubes, dissolved, and spectra were obtained on the DRX 600 equipped with a Cryoprobe.

**Initial NMR data:**

|          | C$_6$H$_7$ | C$_9$H$_{19}$ | C$_7$H$_{13}$Cl |
|----------|------------|---------------|-----------------|
| $^{13}$C NMR peaks (ppm) | 113.90 | 132.35 | 127.58 |
|          | 139.06 | 127.87 | 130.38 |
|          | 132.35 | 127.87 | 132.38 |
| Relative Area | 0.97 | 0.97 | 2.02 |
|          | 0.96 | 0.96 | 1.97 |
|          |       |       | 2.01 |
| Average Area | 0.97 | 0.97 | 2.00/2 = 1.00 |

**Post reaction NMR data:**

|          | C$_6$H$_7$ | C$_9$H$_{19}$ | C$_7$H$_{13}$Cl |
|----------|------------|---------------|-----------------|
| $^{13}$C NMR peaks (ppm) | 113.86 | 132.30 | 127.51 |
|          | 138.97 | 127.84 | 130.37 |
|          | 132.46 |       | 132.46 |
| Relative Area | 0.18 | 0.94 | 2.03 |
|          | 0.18 | 0.92 | 1.95 |
|          |       |       | 2.00 |
| Average Area | 0.18 | 0.93 | 1.99/2 = 1.00 |
| Rel. % of alk-ene remaining | 19 | 96 | 100 |
To an oven dried 5 mL round bottom flask was added a stir bar, (E)-ethyl undec-2-enoate (63.7 mg, 0.30 mmol, 1.5 equiv.), a 1:1 mixture of Z:E-undec-2-ene (74.6 mg, 0.48 mmol, 2.4 equiv.), 2-methylundec-2-ene (50.5 mg, 0.30 mmol, 1.5 equiv.) and 1,2-dichlorobenzene (33.9 µL, 44.1 mg, 0.3 mmol, 1.5 equiv.) under an argon atmosphere. The mixture was stirred vigorously, then 1/3 of the mixture was removed and placed into an NMR tube for the initial starting material ratio (see below). To the remaining material was added isopropanol (0.6 mL), phenylsilane (24.6 µL, 21.6 mg, 0.2 mmol, 1.0 equiv.), and tert-butylhydroperoxide (30.9 µL of 9.7 M in DCM; 44.1 mg, 0.3 mmol, 1.5 equiv.), and the solution was degassed for 10 minutes. Mn(dpm)$_3$ (12.1 mg, 0.02 mmol, 0.10 equiv.) was added and the solution was degassed another 30 seconds. The reaction was then stirred at 500 rpm for 1.0 hours, at which point the reaction was quenched by the addition of NH$_4$OH (1:1 v/v aq., 1.0 mL). The reaction was extracted with hexanes (1x 5 mL) and diethyl ether (1x 5 mL), and the combined organic layer was dried over MgSO$_4$, filtered and concentrated carefully in vacuo to minimize loss of starting material. The resulting brown oil was flushed through a plug of silica (~5 mL) with hexanes (100%) to hexanes/diethyl ether (1:1), and the solution was carefully concentrated to obtain a yellow oil. The resulting oil was placed in an NMR tube. Cr(acac)$_3$ (~8 mg.) was added to both tubes, dissolved, and spectra were obtained on the DRX 600 equipped with a Cryoprobe.

Initial NMR data:

|  | C$_6$H$_{17}$ | C$_6$H$_{17}$ | C$_6$H$_{17}$ | C$_6$H$_{17}$ |  |
|---|---|---|---|---|---|
| $^{13}$C NMR peaks (ppm) | 121.01 | 149.29 | 123.38 | 124.31 | 124.78 | 127.58 | 130.38 | 132.39 |
| Relative Area | 0.85 | 0.83 | 0.70 | 0.73 | 0.67 | 0.71 | 0.88 | 0.83 | 2.01 | 2.00 | 1.98 |
| Average Area | 0.83 | 0.72 | 0.69 | 0.86 | 2.00/2 = 1.00 |
Post reaction NMR data:

| 13C NMR peaks (ppm) | 121.09 | 149.11 | 166.45 | 123.32 | 130.60 | 124.26 | 131.46 | 124.80 | 130.71 | 127.49 | 130.36 | 132.48 |
|---------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Relative Area       | 0.57   | 0.58   | 0.57   | 0.53   | 0.62   | 0.69   | 0.71   | 0.87   | 0.87   | 2.03   | 2.01   | 1.95   |
| Average Area        | 0.57   | 0.58   | 0.70   | 0.87   |        |        |        | 2.00/2 = 1.00 |
| Rel. % of alkene remaining | 69     | 81     | 101    | 101    | 100    |

To an oven dried 5 mL round bottom flask was added a stir bar, (E)-ethyl undec-2-enoate (63.7 mg, 0.30 mmol, 1.5 equiv.), a 1.00:0.54 mixture of E:Z-1-methoxydec-1-ene (78.7 mg, 0.46 mmol, 2.31.0 equiv.), 2-methylundec-2-ene (50.5 mg, 0.30 mmol, 1.5 equiv.) and 1,2-dichlorobenzene (33.9 µL, 44.1 mg, 0.3 mmol, 1.5 equiv.) under an argon atmosphere. The mixture was stirred vigorously, then 1/3 of the mixture was removed and placed into an NMR tube for the initial starting material ratio (see below). To the remaining material was added isopropanol (0.6 mL), phenylsilane (24.6 µL, 21.6 mg, 0.2 mmol, 1.0 equiv.), and tert-butyldihydroperoxide (30.9 µL of 9.7 M in DCM; 44.1 mg, 0.3 mmol, 1.5 equiv.), and the solution was degassed for 10 minutes. Mn(dpm)$_3$ (12.1 mg, 0.02 mmol, 0.10 equiv.) was added and the solution was degassed another 30 seconds. The reaction was then stirred at 500 rpm for 1.0 hour, at which point the reaction was quenched by the addition of NH$_4$OH (1:1 v/v aq., 1.0 mL). The reaction was extracted with hexanes (1x 5 mL) and diethyl ether (1x 5 mL), and the combined organic layer was dried over MgSO$_4$, filtered and concentrated carefully in vacuo to minimize loss of starting material. The resulting brown oil was flushed through a plug of silica (~5 mL) with hexanes (100%) to hexanes/diethyl ether (1:1), and the solution was carefully concentrated to obtain a yellow oil. The resulting oil was placed in an NMR tube. Cr(acac)$_3$ (~8 mg.) was added to both tubes, dissolved, and spectra were obtained on the DRX 600 equipped with a Cryoprobe.
### Initial NMR data:

|                  | Et  | MeO | MeO |       | Cl  |
|------------------|-----|-----|-----|-------|-----|
| **C\textsubscript{13} NMR peaks (ppm)** | 121.05 | 149.24 | 166.54 | 102.97 | 124.80 |
| **Relative Area** | 0.92 | 0.87 | 0.92 | 0.53 | 0.87 |
| **Average Area**  | 0.89 | 0.93 | 0.52 | 0.88 | 2.00 |

### Post reaction NMR data:

|                  | Et  | MeO | MeO |       | Cl  |
|------------------|-----|-----|-----|-------|-----|
| **C\textsubscript{13} NMR peaks (ppm)** | 120.97 | 149.07 | 166.36 | 102.75 | 124.69 |
| **Relative Area** | 0.28 | 0.30 | 0.28 | 0.33 | 0.78 |
| **Average Area**  | 0.29 | 0.98 | 0.35 | 0.80 | 2.15 |
| **Normalized Average Area** | 0.27 | 0.91 | 0.32 | 0.74 | 1.00 |
| **Rel. % of alkene remaining** | 30 | 99 | 62 | 85 | 100 |

To an oven dried 5 mL round bottom flask was added a stir bar, 2-methylundec-2-ene (50.5 mg, 0.30 mmol, 1.5 equiv.), a 1.00:0.54 mixture of E,Z-1-methoxydec-1-ene (78.7 mg, 0.46 mmol, 2.31.0 equiv.), dec-1-yne (58.9 mg, 0.30 mmol, 1.5 equiv.), 2,3-dimethyldodec-2-ene (58.9 mg, 0.30 mmol, 1.5 equiv.) and 1,2-dichlorobenzene (33.9 µL, 44.1 mg, 0.3 mmol, 1.5 equiv.) under an argon atmosphere. The mixture was stirred vigorously, then 1/3 of the mixture was removed and placed into an NMR tube for the initial starting material ratio (see below). To the remaining material was added isopropanol (0.6 mL), phenylsilane (24.6 µL, 21.6 mg, 0.2 mmol, 1.0 equiv.), and tert-butylhydroperoxide (30.9 µL of 9.7 M in DCM; 44.1 mg, 0.3 mmol, 1.5 equiv.), and the solution was degassed for 10 minutes. Mn(dpm)\textsubscript{3} (12.1 mg,
0.02 mmol, 0.10 equiv.) was added and the solution was degassed another 30 seconds. The reaction was then stirred at 500 rpm for 1.0 hours, at which point the reaction was quenched by the addition of NH₄OH (1:1 v/v aq., 1.0 mL). The reaction was extracted with hexanes (1x 5 mL) and diethyl ether (1x 5 mL), and the combined organic layer was dried over MgSO₄, filtered and concentrated carefully in vacuo to minimize loss of starting material. The resulting brown oil was flushed through a plug of silica (~5 mL) with hexanes (100%) to hexanes/diethyl ether (1:1), and the solution was carefully concentrated to obtain a yellow oil. The resulting oil was placed in an NMR tube. Cr(acac)₃ (~8 mg.) was added to both tubes, dissolved, and spectra were obtained on the DRX 600 equipped with a Cryoprobe.

**Initial NMR data:**

| 13C NMR peaks (ppm) | 102.93 | 146.69 | 106.94 | 145.69 | 124.75 | 130.77 | 67.91 | 84.49 | 123.29 | 127.82 | 127.53 | 130.35 | 132.29 |
|----------------------|--------|--------|--------|--------|--------|--------|-------|-------|--------|--------|--------|--------|--------|
| Relative Area        | 0.93   | 0.51   | 0.91   | 0.90   | 0.87   | 0.89   | 0.91  | 0.94  | 2.00   | 1.99   | 2.02   |
| Average Area         | 0.94   | 0.53*  | 0.91   | 0.88*  | 0.93   | 2.00/2 = 1.00 |

| 13C NMR peaks (ppm) | 102.68 | 146.67 | 106.83 | 145.61 | 124.68 | 130.56 | 67.82 | 84.19 | 123.14 | 127.68 | 127.39 | 130.26 | 132.39 |
|----------------------|--------|--------|--------|--------|--------|--------|-------|-------|--------|--------|--------|--------|--------|
| Relative Area        | 1.01   | 0.42   | 0.84   | 0.87   | 0.71   | 0.70   | 0.99  | 0.98  | 2.12   | 2.00   | 1.88   |
| Average Area         | 1.00   | 0.42   | 0.86   | 0.71   | 0.99   | 2.00/2 = 1.00 |
| Rel. % of alkene(yne) remaining | 106 | 79* | 95 | 81* | 106 | 100 |
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SI-93
Δ1,2-24

-158.53
-134.32
-119.82
-116.45
-77.16
-72.83
-33.48
-29.37
-28.59
-23.98
-23.72
Δ1,2-29

H

1 H

1 H

1 H

1 H

1 H

1 H

1 H

1 H

1 H

1 H

1 H

1 H

1 H

1 H

1 H

1 H

1 H

1 H

1 H

1 H

1 H

1 H

1 H

1 H
Initial NMR data:
Post reaction NMR data:

\[ \text{Mn(dpm)}_3 \text{PhSiH}_3 \rightarrow \text{TBHP iPrOH, Ar atm} \]

\[ \text{C}_6\text{H}_{17} \text{OEt} \rightarrow \text{C}_6\text{H}_{17} \text{C}_3\text{H}_{12} \text{OEt} \]
Initial NMR data:
Post reaction NMR data:
Post reaction NMR data:
Initial NMR data:
Post reaction NMR data:
Initial NMR data:
Post reaction NMR data:
Initial NMR data:
Post reaction NMR data:

- **Mn(dpm)$_3$** PhSiH$_3$
- TBHP iPrOH, Ar atm

C$_4$H$_7$OEt

- **f$_1$ (ppm)**
  - 7.0 - 7.1
  - 2.0 - 2.1
  - 1.5 - 1.6

C$_6$H$_7$Cl

- **f$_1$ (ppm)**
  - 7.5 - 7.6

C$_8$H$_17$OEt

- **f$_1$ (ppm)**
  - 4.0 - 4.1

C$_8$H$_17$Cl

- **f$_1$ (ppm)**
  - 7.0 - 7.1

C$_8$H$_17$MeO

- **f$_1$ (ppm)**
  - 3.0 - 3.1

C$_9$H$_17$Cl

- **f$_1$ (ppm)**
  - 7.5 - 7.6

C$_9$H$_17$Cl

- **f$_1$ (ppm)**
  - 7.5 - 7.6
Initial NMR data:
Post reaction NMR data: