Simple, Chemoselective, Catalytic Olefin Isomerization

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Supporting Information

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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. Anhydrous benzene was 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 benzene was distilled from calcium hydride (10 % w/v) under positive pressure of argon. 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 5mm DCH Cryoprobe), AV-600, 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, p = pentet, 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/MS runs were performed with the following method: GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then held for 2 min. GC/FID analysis was conducted on an Agilent 7820A GC/FID system with nitrogen as a carrier gas and with air and hydrogen as combustion gasses. Unless otherwise specified, GC/FID runs were prepared with the following method: GC/FID; HP-5MS UI, Part # 190915-577UI; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then held for 2 min.

Experimental procedures

General Procedure A

A small vial was flame dried under vacuum and degassed under an argon atmosphere for 5 minutes and then charged with the starting material. Another small test tube, also flame dried under vacuum, was charged with catalyst (3 mol%) and degassed for 10 minutes. Benzene was added to the starting material and the Co(SalenᵗʰᵗBu,ᵗᵗBu)Cl pre-catalyst so that the total concentration relative to substrate was 0.1 M. The resulting dark green solution of pre-catalyst was syringed or cannulated into the small vial and phenylsilane (6 mol%) was then added. The reaction rapidly formed a clear red-orange solution and was stirred at room temperature or at 60 °C until completion of the reaction as determined by GC/MS analysis. The reaction mixture was partially evaporated and directly purified by flash chromatography on a silica gel column with Et₂O:hexane as eluent, to furnish the desired product. [Note] Dichloromethane can be a good choice of eluent for non-polar compounds and MeOH (up to 15%) was added for polar compound.

General Procedure B

An oven dried test tube (Fisher Scientific, Borosilicate glass 10x75 mm, Cat. No. 14-961-25) was fitted with a septum and argon gas was then flowed continuously through the test tube. The cobalt pre-catalyst was then added via syringe as a solution in benzene or DCM (at a
concentration of ~0.010 M) and allowed to concentrate to dryness under a flow of argon. Benzene was then added to form a [0.1 M] solution relative to substrate, which was subsequently added via a micro-syringe. The resulting homogeneous solution turned a dark black-green color. Reductant (PhSiH₃) was then added directly via a micro-syringe, which resulted in a distinct color change to a shade of orange or red (with a more red color resulting at higher pre-catalyst loadings), within minutes. In cases where heating was involved, the reaction was placed into a pre-heated oil bath immediately after the addition of phenylsilane. The reaction was then monitored by GC-MS, GC-FID or TLC as was best suited to the properties of the substrate. Upon completion, the reaction was concentrated either partially or completely to dryness by flowing argon/nitrogen over the reaction or was concentrated in vacuo for larger scale reactions. The resulting residue was then suspended in an appropriate solvent or loaded directly onto silica and eluted with an appropriate solvent system.

Of practical note: The order of additions is unimportant. The only crucial point is that oxygen be excluded from the reaction. Otherwise, the substrate, pre-catalyst, solvent and reductant may be added in any order as is convenient without any noticeable effect on the success of the reaction. Standard solutions were used to ensure accurate addition of reagents for small-scale reactions, but the reaction works just as well if the reagents are added as solids as long as the reaction vessel is degassed after addition. Also, anhydrous solvent is not normally necessary for the reaction to work well. Sluggish reactions may be heated, and for this purpose mesitylene may also be used although none of the substrates included in this paper required such forcing conditions. Cobalt complexes which differ by the type of axial ligand (F, OAc, OTs) work qualitatively just as well, though the rate of reduction of cobalt by the silane when fluorine is the axial ligand is faster, as observed by the rapidity of the color change.

Cobalt Complexes

The Co(III)salen complexes were prepared according to the procedures of the Jacobsen group. See J. Am. Chem. Soc. 2013, 135, 15595; J. Am. Chem. Soc. 2002, 124, 1307.

Tables

Data included in Tables 1 and 2 below were obtained via GC-FID by comparison of the distribution of products at T=0 with T=X, where X equals the time in hours indicated below. 1,2-dichlorobenzene was used as an internal standard to correct for sampling error. Calibration curves of the alkenes 1 and 2 and hydrocarbon 3 below were made to correct for differences in response factor. All reactions were run with 5 mg. (0.0297 mmol.) of alkene 1 substrate at a concentration of 0.1 M unless otherwise noted.

S.I. Table 1. Distribution of products from common Mukaiyama hydrofunctionalization catalysts.
Comments on entries above:

1) Conditions reported in this manuscript.
2) Conditions reported in *J. Am. Chem. Soc.*, 2014, 136, 1300, but with TBHP excluded.
3) Conditions reported in *J. Am. Chem. Soc.*, 2012, 134,13588 but with i-PrOH added to solubilize the substrate. A precipitate formed during the course of the reaction and this may account for the poor mass balance observed for this reaction.
4) Conditions reported in *J. Am. Chem. Soc.*, 2014, 136, 1304
5) Same as for entry 4 but with benzene as the solvent.
6) Conditions of the general procedure but using Co(acac)$_3$.
7) SalcomineCl is catalyst E from S.I. Table 3 (below).
8) Conditions reported in this manuscript.
9) Conditions reported in this manuscript. The reaction continues to higher conversion if given more time.
10) Conditions reported in this manuscript. Excess PMHS was required to reach high conversion.
11) Conditions reported in this manuscript. No reaction was observed.
12) A solid precipitate forms during the course of the reaction. Presumably, AIBN also reacts with the [Co] catalyst to form an insoluble precipitate.

S.I. Table 2. Control Experiments pertinent to the contents of Table 1

| entry | conditions$^a$ | %1 $^b$ | %2 | %3 |
|-------|----------------|---------|-----|-----|
| 1     | 1 mol% Co(Sal$^\text{Bu,}^\text{tBu}$)Cl, 2 mol% PhSiH$_3$, PhH, 22 °C, 3 h | 4 | 96 | 0 |
| 2     | 10 mol% Mn(dpm)$_3$, 2 equiv. PhSiH$_3$, i-PrOH, 22 °C, 3 h | 39$^c$ | 0 | 16 |
| 3     | 2 equiv. Fe$_2$(oxalate)$_3$, 6.4 equiv. NaBH$_4$, ACN/H$_2$O/i-PrOH (1:1:0.2), 0 °C, 1 h, air atm. | 34 | 1 | 1 |
| 4     | 50 mol% Fe(acac)$_3$, 1 equiv. PhSiH$_3$, EtOH, 60 °C, 1 h | 28$^c$ | 0 | 57 |
| 5     | 50 mol% Fe(acac)$_3$, 1 equiv. PhSiH$_3$, PhH, 60 °C, 1 h | 65$^c$ | 0 | 0 |
| 6     | 50 mol% Co(acac)$_3$, 1 equiv. PhSiH$_3$, PhH, 60 °C, 1 h | 99 | 0 | 0 |
| 7     | 5 mol% Salcomine-Cl, 50 mol% PhSiH$_3$, PhH, 60 °C, 3 h | 65 | 20 | 6 |
| 8     | 1 mol%, Co(Sal$^\text{Bu,}^\text{tBu}$)Cl, 10 mol% PhSiH$_3$, Me$_2$CO, 22 °C, 3 h. | 5 | 94 | <1 |
| 9     | 1 mol% Co(Sal$^\text{Bu,}^\text{tBu}$)Cl, 10 mol% PhSiH$_3$, CH$_2$Cl$_2$, 22 °C, 3 h | 17$^c$ | 63 | 2 |
| 10    | 5 mol% Co(Sal$^\text{Bu,}^\text{tBu}$)Cl, 2 equiv. PMHS, PhH, 22 °C, 24 h | 4$^c$ | 78 | 0 |
| 11    | 2 mol% Co(Sal$^\text{Bu,}^\text{tBu}$)Cl, 40 mol% TESH, PhH, 22 °C, 24 h | 98 | 0 | 0 |
| 12    | 5 mol% Co(Sal$^\text{Bu,}^\text{tBu}$)Cl, 50 mol% AIBN, PhH, 80 °C, 2 h | 86 | 11 | 0 |

$^a$under Ar unless otherwise noted; $^b$according to GC-FID; $^c$other unidentified product(s) were observed.
S.I. Table 3. Cycloisomerization vs. Isomerization

These experiments were run using general procedure B and analyzed by GC-FID. 1,2-dichlorobenzene was added as an internal standard to correct for sampling errors. In each case, there were other unidentified peaks, so it must be noted that the conversion of starting material is not necessarily to products 6 and 27, although these were the major products.
The control experiments in which compound 27 was treated under the same experimental conditions as entries 1-6 showed 100% starting material remaining after 24 hours, ruling out conversion of 27 to 6 as a possible pathway.

**Isomerization**

![2-methylundec-1-ene (Table 2, Entry 1)]

2-methylundec-1-ene (Table 2, Entry 1)
The title compound was prepared by a Wittig reaction of undecan-2-one. A flame-dried 250 mL round bottom flask was charged with 19.1 mmol (1.2 eq.) of methyl triphenyl phosphonium bromide, a stir bar and anhydrous diethyl ether (100 mL). A reflux condenser was attached and the suspension was placed under an Argon atmosphere. To this was added 1.2 eq. of a 1M solution of KOt-Bu in THF, which resulted in a bright yellow solution. The reaction was heated at reflux for 30 minutes. Undecan-2-one (15.4 mmol, 1.0 eq.) as a solution in 40 ml of anhydrous diethyl ether was then added dropwise. The reaction was monitored by TLC and after 4 hours was found to be complete. The reaction was concentrated directly by rotary evaporation, suspended in pentanes and filtered by suction filtration through a thick plug of silica. The solution was concentrated once more, suspended again in pentanes and filtered through a plug of silica to remove the small amount of triphenyl phosphine oxide remaining. The desired product was obtained as a clear colorless oil in 95% yield (14.6 mmol) after removal of solvent in vacuo. The spectral data obtained matched those previously reported.

Pandey, S. K.; Greene, A. E.; Poisson, J.-F. *J. Org. Chem.* 2007, 72, 7769-7770

![2-methylundec-2-ene (Table 2, Entry 1)]

2-methylundec-2-ene (Table 2, Entry 1)
Using general procedure B with the following modifications gave the title compound (18.2 mg, 0.108 mmol) as a clear colorless oil in 91% yield after FCC purification through silica with 100% pentanes.
- temperature: rt
- salenCoCl: 2 mol%
- PhSiH₃: 2 mol%
Spectral information obtained matched those previously reported
Rao Volla, C. M.; Vogel P. *Angew. Chem. Int. Ed.* 2008, 47, 1305-1307

![1-decene (Table 2, Entry 2)]

1-decene (Table 2, Entry 2)
The title compound was purchased from Alfa Aesar in 96% purity, with the remainder being isomers. Spectral information obtained matched those previously reported.
Furayama, T.; Yonehara, M.; Arimoto, S.; Kobayasi, M.; Matumoto, Y.; Uchiyama, M. Chem. Eur. J. 2008, 14, 10348-10356

(E/Z)-dec-2-ene (Table 2, Entry 2)
Using general procedure B with the following modifications gave the title compound (8.3 mg, 0.060 mmol) as a clear colorless oil in 83 % yield after FCC purification through silica with 100% pentanes.
-temperature: 60 °C
-salenCoCl: 5 mol%
-PhSiH₃: 50 mol%
The spectral data obtained matched those previously reported.
For E-isomer, see: Reddy, M. R.; Periasamy, M. J. Orgmet. Chem. 1995, 491, 263.
For Z-isomer, see: Belger, C., Neisius N.M., Plietker, B., Chem. Eur. J. 2010, 16, 12214.
The ratio of E:Z:sum of 4 other isomers was found to be 66:20:14 by GC-FID.

(E)-2,6,10-trimethylundeca-1,5,9-triene (Table 2, Entry 3)
The title compound was prepared by a Wittig reaction of geranyl acetone using the same procedure as 2-methylundec-1-ene (above) with the following modifications.
Substrate: 1.0 eq. 5.15 mmol., 1.0 g.
Ph₃PMeBr: 1.1 eq., 2.02 g.
KOt-Bu: (1M in THF), 1.1 eq., 5.66 mL
Et₂O (anhydrous): 40 mL + 10 mL
The spectral data obtained matched those previously reported.
Takai, K., Hotta, Y., Oshima, K., Nozaki, H. Bull. Chem. Soc. Jpn., 1980, 53, 1698.

2,6-dimethylhepta-2,5-diene (Table 2, Entry 3)
Using general procedure B with the following modifications gave the title compound (9.8 mg, 0.051 mmol) as a clear colorless oil in 65% yield after purification. Purification consisted of first removing the [Co] complex by flushing the reaction residue through a plug of silica with pentanes followed by preparatory TLC on plates pretreated with a 10% solution of AgNO₃ in acetonitrile.
-temperature: rt
-salenCoCl: 5 mol%
-PhSiH₃: 10 mol%
Spectral information obtained matched those previously reported.

Zilenovski, J. S. R., Hall, S. S., J. Org. Chem., 1979, 44(7), 1159.

\[
\begin{align*}
\text{(3-methylbut-3-enyl)benzene (Table 2, Entry 4)}
\end{align*}
\]

The title compound was prepared by a previously reported procedure and the spectral data obtained matched those previously reported.

Lebel, H.; Guay, D.; Paquet, V.; Huard, K. Org. Lett. 2004, 6, 3047.

\[
\begin{align*}
\text{(3-methylbut-2-enyl)benzene (Table 2, Entry 4)}
\end{align*}
\]

Using general procedure A with the following modifications gave the title compound (41.6 mg, 0.284 mmol) as a clear yellow oil in 83 % yield.

-temperature: rt.
-salenCoCl: 3 mol% (6.74 mg 0.0102 mmol)
-PhSiH\textsubscript{3}: 6 mol% (2.50 μL, 0.0204 μmol)

Spectral information obtained matched those previously reported.

Ohmiya, H.; Makida, Y.; Tanaka, T.; Sawamura, M. J. Am. Chem. Soc. 2008, 130, 17276.

\[
\begin{align*}
\text{(S)-(4,6-dimethylhept-1-en-2-yl)cyclopentane (Table 2, Entry 5)}
\end{align*}
\]

The title compound was made from (S)-citronellal by the following sequence:

To a solution of cyclopentyl magnesium chloride (2M in Et\textsubscript{2}O) (6.6 mmol, 1.1 eq.) in anhydrous THF (10 mL) was added a solution of (S)-citronellal (1.0 eq., 6.0 mmol) in 5 mL of anhydrous THF. The reaction was monitored by TLC and upon completion, the reaction mixture was isolated by pouring the solution into 5 mL of ice cold 1 N HCl, extracting with diethyl ether (3x ~5 mL), drying over MgSO\textsubscript{4}, and concentrating \textit{in vacuo}.

Next, the crude alcohol was added to a suspension of Pd/C (10% w/w) and degassed with argon for 15 minutes to remove oxygen from the system. Hydrogen gas was bubbled through the solution until the reaction was complete, determined by GC-MS. The suspension was filtered through a plug of celite, rinsing with MeOH. The resulting mixture was concentrated \textit{in vacuo} and purified by FCC on silica in 10% EtOAc/hex to obtain a mixture of diastereomers in 95% yield (1.28 g.; over 2 steps).

To a flame dried 5 mL round bottom flask containing a stir bar, NaOAc (15.4 mg, 0.1 eq.), DCM (15 mL), the diastereomeric mixture of alcohols (1.0 eq., 1.88 mmol) and 4Å molecular sieves
was added PCC (1.7 eq., 3.27 mmol) while stirring. The reaction changed colors from from orange to a blackish orange shade during the course of the reaction. The progress of the reaction was monitored by TLC. Upon completion, the reaction was filtered through florisil to obtain a clear green solution which was subsequently concentrated in vacuo and purified by FCC over silica with 10% EtOAc/hex to obtain the desired ketone as a pale yellow oil in 66% yield (278 mg).

The isolated ketone (1.0 eq., 278 mg, 1.24 mmol) was converted to (S)-(4,6-dimethylhept-1-en-2-yl)cyclopentane via a Wittig reaction using the same procedure as for 2-methylundec-1-ene above except that 1.3 equivalents of KOTBu and methyl triphenyl phosphonium bromide were used. The title compound was obtained in 99% yield (275 mg., 1.23 mmol) as a clear pale yellow oil.

\[ \text{1H NMR (400 MHz, Chloroform-}d\text{) } \delta 4.85 - 4.74 (m, 1H), 4.71 - 4.63 (m, 1H), 2.42 - 2.26 (m, 1H), 2.09 (dd, J = 14.0, 5.9, 1H), 1.89 - 1.75 (m, 3H), 1.75 - 1.48 (m, 5H), 1.48 - 1.20 (m, 5H), 1.20 - 1.02 (m, 3H), 0.87 (d, J = 6.5 Hz, 6H), 0.85 (d, J = 6.5 Hz, 3H). \]

\[ \text{13C NMR (101 MHz, CDCl}_3\text{) } \delta 152.25, 107.92, 45.72, 44.48, 39.50, 37.52, 31.93, 31.70, 31.13, 28.17, 25.10, 25.06, 25.04, 22.89, 22.78, 19.82. \]

(GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min): \( t_R = 6.735 \text{ min.} \)

\[ \text{m/z calcd for } 222.2348 \text{ MS (EI, 70 eV): } m/z (\%) 222.3 (10), 137.2 (17), 111.1 (55), 110.1 (45), 109.1 (40), 97.1 (34), 96.1 (60), 95.1 (69), 83.1 (22), 82.1 (21), 81.1 (56), 79.1 (21), 71.1 (27), 70.1 (15), 69.1 (67), 68.1 (29), 67.1 (100), 66.1 (25), 57.1 (53), 56.1 (30), 55.1 (50) \]

(S)-(4,6-dimethylheptan-2-ylidene)cyclopentane (Table 2, Entry 5)

Using general procedure B with the following modifications gave the title compound (9.1 mg, 0.041 mmol) as a clear yellow oil in 91% yield.

- Temperature: 22 °C
- salenCoCl: 1 mol%
- PhSiH\(_3\): 2 mol%

\[ \text{1H NMR (600 MHz, Chloroform-}d\text{) } \delta 2.18 (m(b), 4H), 1.95 (dd, J = 13.1, 6.1 Hz, 1H), 1.82 (dd, J = 13.2, 8.4 Hz, 1H), 1.67-1.45 (m, 6 H), 1.40-1.00 (m, 9 H) 0.87 (m, 0.81, 6H) (d, J = 6.6, 3H). \]

\[ \text{13C NMR (101 MHz, CDCl}_3\text{) } \delta 137.38, 124.56, 43.50, 39.51, 37.51, 31.81, 30.87, 30.79, 28.18, 27.19, 26.90, 25.19, 22.90, 22.79, 19.70, 19.20. \]

(GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min): \( t_R = 6.878 \text{ min.} \)

\[ \text{m/z calcd for } 222.2348 \text{ MS (EI, 70 eV): } m/z (\%) 222.3 (18), 110.1 (27), 109.1 (100), 108.1 (19), 96.1 (39), 95.1 (18), 93.1 (16), 81.1 (17), 67.1 (54), 55.1 (16) \]
methyl 2-methylenepentanoate (Table 2, Entry 6)
The title compound was prepared by a previously reported procedure, highlighted in the preceding scheme and the spectral data obtained matched those previously reported.
Yang, K.-W.; Golich, F. C.; Sidgel, T. K.; Crowder, M.W. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 5150.

methyl 2-methylpent-2-enoate (Table 2, Entry 6)
Using general procedure A with the following modifications gave the title compound (80 mg, 0.39 mmol; E/Z > 10:1) as a clear yellow oil in 69% yield.
- temperature: 60 °C
- salenCoCl: 5 mol%
- PhSiH3: 10 mol%
Liu, Y.; Mao, D.; Xu, D.; Zhenyuan, Z.; Zhang, Y. *Synth. Comm.* **2007**, *37*, 4389-4397

((3-methylbut-3-enyloxy)methyl)benzene (Table 2, Entry 7)
The title compound was prepared by a previously reported procedure and the spectral data obtained matched those previously reported.
Cleary, P. A.; Woerpel, K. A. *Org. Lett.* **2005**, *7*, 5531.

((3-methylbut-2-enyloxy)methyl)benzene (Table 2, Entry 7)
Using general procedure A with the following modifications gave the title compound (38.7 mg, 0.220 mmol) as a clear yellow oil in 77 % yield.
- temperature: rt
- salenCoCl: 3 mol% (4.34 mg, 0.00660 mmol)
- PhSiH3: 6 mol% (1.70 μL, 0.0132 mmol)
Spectral information obtained matched those previously reported
Bourque, L.E.; Cleary, P. A.; Woerpel, K. A. *J. Am. Chem. Soc.* **2007**, *129*, 12602-12603.

((2-methylallyloxy)methyl)benzene (Table 2, Entry 8)
The title compound was prepared by a previously reported procedure and the spectral data obtained matched those previously reported.
Blanc, A.; Toste D. F. *Angew. Chem. Int. Ed.* **2006**, *45*, 2096-2099
**((2-methylprop-1-enyloxy)methyl)benzene (Table 2, Entry 8)**

Using general procedure A with the following modifications gave the title compound (40.5 mg, 0.250 mmol) as a yellow oil in 81% yield.

- temperature: rt
- salenCoCl: 3 mol% (4.92 mg, 0.0075 mmol)
- PhSiH₃: 6 mol% (2.00 μL, 0.0150 mmol)

Spectral information obtained matched those previously reported by Bourque, L.E.; Cleary, P. A.; Woerpel, K. A. *J. Am. Chem. Soc.* **2007**, **129**, 12602-12603.

**2-methylene propane-1,3-diol bis (tert-butylidimethylsilane) (Table 2, Entry 9)**

The title compound was prepared by a previously reported procedure and the spectral data obtained matched those previously reported by Gaydou, M.; Miller, R. E.; Delpont, N.; Ceccon, J.; Echavarren, A. M. *Angew. Chem. Int. Ed.* **2013**, **52**, 6396-6399.

**2-methylprop-1-ene-1,3-diol bis (tert-butylidimethylsilane) (Table 2, Entry 9)**

Using general procedure A with the following modifications gave the title compound (46.0 mg, 0.145 mmol) as a clear yellow oil in 92% yield and as a mixture of diastereomers (1 : 2.56)

- temperature: 60 °C
- salenCoCl: 5 mol% (4.76 mg, 0.00725 mmol)
- PhSiH₃: 10 mol% (2.00 μL, 0.0145 mmol)

**1H NMR** (600 MHz, Chloroform-d) δ 6.26 (s, 1H), 6.02 (s, 1H), 4.26 (d, J = 1.0 Hz, 2H), 3.99 (d, J = 1.1 Hz, 2H), 1.62 (d, J = 1.4 Hz, 3H), 1.58 (d, J = 1.4 Hz, 3H), 0.97 - 0.93 (m, 9H), 0.93 – 0.90 (m, 9H), 0.14 (d, J = 6.7 Hz, 6H), 0.08 (d, J = 3.7 Hz, 6H).

**13C NMR** (151 MHz, CDCl₃) δ 136.28, 134.73, 117.04, 116.66, 65.69, 59.60, 26.11, 25.79, 18.56, 18.35, -5.01, -5.12

**GC (GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min): tR = 6.867 min and 6.924 min.**

m/z calcd for C₁₆H₃₆O₂Si(M)^+ 316.2254

**MS (EI, 70 eV):** m/z (%) 316.3(1), 259.2 (23), 148.1 (16), 147.1 (100), 133.1(14), 74.1 (6), 73.1 (69)

**MS (EI, 70 eV):** m/z (%) 316.2 (1), 259.2 (14), 185.2 (13), 147.1 (100), 133.1 (11), 75.1 (17), 74.1 (4), 73.1 (47)

**3-methyl-6-(2-methylallyl)cyclohex-2-enone (Table 2, Entry 10)**

A flame dried round bottom flask charged with diisopropylamine (1.1 eq) and THF (0.2 M) was cooled down to -78 °C under argon atmosphere. A solution of n-BuLi (1.6 M in hexanes, 1.05
eq) was added slowly to this solution at −78 °C and stirred for 45 min. 3-methylcyclohex-2-enone (1 eq.) was added and the mixture was stirred for another 45 minutes at −78 °C. 3-bromo-2-methylpropene (1.1 eq) was then added at −78 °C and the reaction was stirred 3 h and slowly warmed-up to room temperature. An aqueous saturated solution of NH₄Cl was added and the aqueous layers were extracted with ethyl acetate (3x). The combined organic phases were dried over anhydrous magnesium sulfate, filtered and the solvent was evaporated. The crude residue was purified by flash chromatography on a short silica gel column with 10% Et₂O: hexane to furnish a clear oil in 78% isolated yield.

**1H NMR** (600 MHz, Chloroform-d) δ 5.86 (q, J = 1.4 Hz, 1H), 4.80 (ddt, J = 2.9, 2.1, 1.1 Hz, 1H), 4.70 (ddt, J = 2.4, 1.6, 0.9 Hz, 1H), 2.66 (dd, J = 14.2, 3.9 Hz, 1H), 2.35 (tt, J = 10.4, 4.4 Hz, 1H), 2.29 (dddd, J = 7.8, 3.9, 1.8, 0.9 Hz, 2H), 2.06 (dq, J = 13.6, 4.9 Hz, 1H), 1.99 – 1.95 (m, 1H), 1.95 (q, J = 1.0 Hz, 3H), 1.71 (dt, J = 1.6, 0.8 Hz, 3H), 1.68 – 1.56 (m, 1H)

**13C NMR** (151 MHz, CDCl₃) δ 201.30, 161.83, 143.56, 126.39, 112.50, 43.22, 37.73, 30.20, 26.97, 24.35, 22.06

GC (GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min): tR = 5.705 min. m/z calcd for C₁₁H₁₆O (M)⁺ 164.1201

**MS** (EI, 70 eV): m/z (%) 164.1 (33), 109.1 (22), 108.1 (13), 82.1 (100), 67.1 (16), 54.1 (11), 53.1 (10)

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3-methyl-6-(2-methylprop-1-enyl)cyclohex-2-enone (Table 2, Entry 10)

Using general procedure A with the following modifications gave the title compound (37.1 mg, 0.226 mmol) as a clear yellow oil in 74 % yield.

-temperature: rt
-salenCoCl: 5 mol% (7.42 mg 0.0113 mmol)
-PhSiH₃: 10 mol% (2.75 μL, 0.0226 mmol)

**1H NMR** (400 MHz, Chloroform-d) δ 5.86 (s, 1H), 5.18 (ddq, J = 8.8, 2.9, 1.4 Hz, 1H), 3.10 (ddd, J = 10.8, 8.7, 4.8 Hz, 1H), 2.33 (dddt, J = 6.0, 4.9, 3.0, 1.1 Hz, 2H), 2.08 – 1.97 (m, 1H), 1.94 (s, 3H), 1.88 – 1.76 (m, 1H), 1.74 (s, 3H), 1.65 (s, 3H).

**13C NMR** (151 MHz, CDCl₃) δ 200.48, 161.63, 135.39, 126.48, 121.56, 45.66, 30.34, 29.54, 26.02, 24.35, 18.28

GC (GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min): tR = 5.928. m/z calcd for C₁₁H₁₆O (M)⁺ 164.1201

**MS** (EI, 70 eV): m/z (%) 164.2 (44), 82.1 (100), 67.1 (32), 54.1 (8)

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**Cycloisomerization**

![Cycloisomerization reaction](image)
diethyl 2-allyl-2-(3-methylbut-2-enyl)malonate (SI 1)
The title compound was prepared by a previously reported procedure and the spectral data obtained matched those previously reported.
Necas, D.; Tursky, M.; Kotora, M. J. Am. Chem. Soc. 2004, 126, 10222-10223.

diethyl 3-methyl-4-(prop-1-en-2-yl)cyclopentane-1,1-dicarboxylate (4)
Using general procedure A with the following modifications gave the title compound (40.7 mg, 0.152 mmol) as a mixture of diastereomers (1 : 5.5 trans : cis) as a clear yellow oil in 82 % yield:
-temperature: 60 °C
-salenCoCl: 5 mol% (6.12 mg 0.00932 mmol)
-PhSiH₃: 10 mol% (2.30 μL, 0.0186 mmol)
¹H NMR (600 MHz, Chloroform-d) δ 4.84 – 4.80 (m, 1H), 4.67 (d, J = 2.1 Hz, 1H), 4.22 – 4.08 (m, 4H), 2.58 – 2.50 (m, 2H), 2.37 – 2.25 (m, 2H), 2.03 (dd, J = 14.0, 2.6 Hz, 1H), 1.71 (s, 3H), 1.69 – 1.63 (m, 1H), 1.28 – 1.16 (m, 6H), 0.70 (d, J = 7.2 Hz, 3H).
¹³C NMR (151 MHz, CDCl₃) δ 194.49, 173.17, 172.96, 144.72, 110.50, 61.53, 61.48, 49.43, 41.24, 35.24, 34.67, 23.22, 15.51, 14.17.
GC (GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min): tR = 7.450 min.
m/z calcd for C₁₅H₂₄O₄ (M)⁺ 268.1675
MS (EI, 70 eV): m/z (%) 268.2 (4), 194.2 (100), 177.1 (18), 173.1¹ (30), 149.1 (8), 120.1 (28), 107.1 (22), 93.1 (29)
MS (EI, 70 eV): m/z (%) 268.1 (1), 194.2 (72), 177.1 (17), 173.1 (22), 127.1 (20), 121.1 (100), 120.2 (22), 93.1 (25), 79.1 (18)

diethyl 2-(2-methylallyl)-2-(3-methylbut-2-enyl)malonate (SI 2)
The title compound was prepared by a previously reported procedure and the spectral data obtained matched those previously reported. Wasson, B. K. Can. J Chem. 1963, 41, 3070-3073.

diethyl 3,3-dimethyl-4-(prop-1-en-2-yl)cyclopentane-1,1-dicarboxylate (5)
Using general procedure A with the following modifications gave the title compound (47.2 mg, 0.166 mmol) as a clear oil in 94 % yield.

- temperature: rt
- salenCoCl: 3 mol% (3.49 mg, 0.00531 mmol)
- PhSiH₃: 6 mol% (1.30 μL, 0.0106 mmol)

¹H NMR (600 MHz, Chloroform-d) δ 4.88 (s, 1H), 4.70 (dd, J = 1.9, 1.0 Hz, 1H), 4.25 – 4.04 (m, 4H), 2.52 – 2.39 (m, 1H), 2.39 – 2.24 (m, 2H), 2.24 – 2.10 (m, 2H), 1.74 (s, 3H), 1.23 (td, J = 7.1, 2.9 Hz, 6H), 1.09 (s, 3H), 0.79 (s, 3H)

¹³C NMR (151 MHz, CDCl₃) δ 173.19, 172.49, 143.73, 112.54, 61.54, 57.58, 55.11, 49.02, 41.78, 37.70, 29.27, 23.70, 14.12

GC (GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min): tR = 7.4224 min.

m/z calcd for C₁₆H₂₆O₄ (M)⁺ 282.1831

MS (EI, 70 eV): m/z (%) 282.2 (1), 263.2 (19), 208.2 (30), 181.1 (26), 169.1 (21), 137.1 (29), 136.1 (21), 135.1 (100), 122.1 (35), 109.1 (27)

diethyl 2-(3-methylbut-2-enyl)-2-(3-methylbut-3-enyl)malonate (SI 3)

In a flame dried round bottom flask charged with sodium hydride (1.05 eq) was added some THF under argon atmosphere. Diethyl 2-(3,3-dimethylallyl)malonate (1 eq.) in DMF was added to this suspension at 0 °C and the mixture was stirred during 30 minutes. 4-iodo-2-methylbut-1-ene (1.1 eq) was finally added and the reaction was stirred for 15 minutes and heated at 70 °C until completion of the reaction. The reaction was quenched with water and worked-up with an aqueous solution of NaHCO₃ (sat.) and Et₂O. The organic phase was dried over magnesium sulfate, filtered and evaporated off. The crude residue was purified by flash chromatography on a short silica gel column with 3% Et₂O:hexane to furnish a clear oil in 77%.

¹H NMR (600 MHz, Chloroform-d) δ 4.94 (ddddd, J = 7.5, 6.1, 2.9, 1.5 Hz, 1H), 4.69 (s, 1H), 4.7 (s, 1H), 4.16 (tttd, J = 15.5, 7.6, 3.8 Hz, 4H), 2.83 – 2.32 (m, 2H), 2.13 – 1.91 (m, 2H), 1.91 – 1.76 (m, 2H), 1.70 (s, 3H), 1.67 (s, 3H), 1.61 (s, 3H), 1.23 (t, J = 7.0 Hz, 6H)

¹³C NMR (151 MHz, CDCl₃) δ 171.66, 145.16, 135.45, 117.84, 110.32, 61.75, 57.46, 32.34, 31.05, 30.50, 26.12, 22.57, 18.05, 14.21

GC (GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min): tR = 7.857 min. m/z calcd for C₁₇H₂₈O₄ (M)⁺ 296.1988

MS (El, 70 eV): m/z (%) 296.3 (1), 228.2 (22), 227.2 (39), 223.2 (39), 222.3 (21), 183.1 (39), 181.1 (71), 160.1 (23), 136.1 (82), 135.2 (100), 127.0 (55), 101.1 (48), 107.1 (25), 95.1 (20), 79.1 (35), 69.1 (64), 67.1 (26)
diethyl 4,4-dimethyl-3-(prop-1-en-2-yl)cyclohexane-1,1-dicarboxylate (6)
Using general procedure A with the following modifications gave the title compound (42.7 mg, 0.144 mmol) as a clear yellow oil in 85% yield and as an inseparable mixture with the compound 30 (2.9:1.0).
-temperature: 3 mol% (3.33 mg, 0.00506 mmol)
-salenCoCl: 3 mol% (3.33 mg, 0.00506 mmol) + 3 mol% (3.33 mg, 0.00506 mmol)
-PhSiH₃: 6 mol% (1.20 μL, 0.0101 mmol) + 6 mol% (1.20 μL, 0.0101 mmol)

¹H NMR (600 MHz, Chloroform-d) δ 4.87 (p, J = 1.7 Hz, 1H), 4.68 – 4.61 (m, 1H), 4.32 – 4.08 (m, 4H), 2.57 (dt, J = 7.4, 1.4 Hz, 1H), 2.26 – 2.15 (m, 1H), 2.12 (dt, J = 7.4, 2.7 Hz, 1H), 1.99 – 1.91 (m, 1H), 1.86 (ddd, J = 13.8, 11.8, 6.3 Hz, 2H), 1.63 – 1.53 (m, 1H), 1.41 – 1.29 (m, 3H), 1.31 – 1.16 (m, 6H), 0.90 (s, 3H), 0.87 (s, 3H)

¹³C NMR (151 MHz, CDCl₃) δ 172.67, 171.32, 146.63, 113.08, 77.37, 61.48, 61.17, 49.77, 38.99, 33.25, 32.57, 31.08, 30.93, 27.26, 24.25, 20.25, 14.26, 14.18.

GC (GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min): tR = 8.086 min.
m/z calcd for C₁₇H₂₈O₄ (M)⁺ 296.1988

MS (EI, 70 eV): m/z (%) 296.2 (6), 223.0 (23), 307.2 (18), 173.1 (30), 153.1 (19), 127.1 (20, 107.1 (17), 93.1 (22)

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diethyl 2,2-bis(3-methylbut-2-ényl)malonate (30)
Using general procedure A with the following modifications gave the title compound (42.7 mg, 0.144 mmol) as a clear yellow oil in 85% yield and as an inseparable mixture with the compound 30 (1:0 : 2.9).
-temperature: 3 mol% (3.33 mg.00506 mmol)
-salenCoCl: 3 mol% (3.33 mg.00506 mmol) + 3 mol% (3.33 mg.00506 mmol)
-PhSiH₃: 6 mol% (1.20 μL, 0.0101 mmol) + 6 mol% (1.20 μL, 0.0101 mmol)

¹H NMR (600 MHz, Chloroform-d) δ 4.95 (ddq, J = 8.9, 6.1, 1.4 Hz, 2H), 4.15 (q, J = 7.1 Hz, aH), 2.57 (dt, J = 7.3, 1.4 Hz, 4H), 1.67 (s, 6H), 1.59 (s, 6H), 1.22 (t, J = 7.2 Hz, 6H).

¹³C NMR (151 MHz, CDCl₃) δ 171.68, 135.35, 118.12, 61.16, 57.81, 30.92, 26.17, 18.00, 14.21

GC (GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min): tR = 7.897 min.
m/z calcd for C₁₇H₂₈O₄ (M)⁺ 296.1988

MS (EI, 70 eV): m/z (%) 296.2 (1), 227.2 (34), 183.1 (12), 181.1 (50), 137.1 (15), 136.1 (25), 79.2 (15), 69.1 (28)

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diethyl 2-(2-cyclohexylideneethyl)-2-(2-methylallyl)malonate (SI 4)
In a flame dried round bottom flask charged with sodium hydride (1.05 eq) was added some THF under argon atmosphere. Diethyl 2-(2-cyclohexylideneethyl)malonate (1 eq.) in DMF was
added to this suspension at 0 °C and the mixture was stirred during 30 minutes. 3-bromo-2-methylpropene (1.1 eq) was finally added and the reaction was stirred until completion of the reaction. The reaction was quenched with water and worked-up with an aqueous solution of NaHCO₃ sat. and Et₂O. The organic phase was dried over magnesium sulfate, filtered and evaporated off. The crude residue was purified by flash chromatography on a short silica gel column with 3% Et₂O:hexane to furnish a clear oil in 77%.

**¹H NMR** (600 MHz, Chloroform-d) δ 5.02 – 4.88 (m, 1H), 4.84 (s, 1H), 4.73 (s, 1H), 4.16 (qq, J = 7.0, 3.7 Hz, 4H), 2.68 (d, J = 1.0 Hz, 2H), 2.64 (d, J = 7.4 Hz, 2H), 2.17 – 2.08 (m, 2H), 2.05 (t, J = 5.8 Hz, 2H), 1.76 – 1.64 (m, 3H), 1.56 – 1.36 (m, 6H), 1.24 (t, J = 7.1 Hz, 6H).

**¹³C NMR** (151 MHz, CDCl₃) δ 171.69, 143.30, 140.98, 115.44, 114.74, 61.27, 57.41, 39.98, 37.59, 30.13, 29.06, 28.70, 27.87, 26.96, 23.51, 14.13

GC (GC/MSD; HP-5MS UI; 139 KPα; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min): tR = 9.413 min. m/z calcd for C₁₉H₃₀O₄ (M)⁺ 322.2144

**MS** (EI, 70 eV): m/z (%) 322.3 (2), 248.2 (52), 175.2 (58), 174.1 (35), 173.1 (45), 166.1 (31), 165.1 (30), 149.1 (29), 122.1 (100), 119.1 (31), 83.1 (22), 81.1 (79.1), 67.2 (63)

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Using general procedure A with the following modifications gave the title compound (43.3 mg, 0.134 mmol) as white brownish solid in 86 % yield. silica gel column was neutralized with Et₃N -temperature: 60 °C
-salenCoCl: 3 mol% (3.05 mg 0.00465 mmol)
-PhSiH₃: 6 mol% (1.10 μL, 0.00930 mmol)

**¹H NMR** (600 MHz, Chloroform-d) δ 5.42 (dt, J = 3.6, 2.4 Hz, 1H), 4.33 – 3.95 (m, 4H), 2.45 (t, J = 13.4 Hz, 1H), 2.34 – 2.21 (m, 1H), 2.21 – 2.06 (m, 3H), 2.06 – 1.94 (m, 3H), 1.89 (q, J = 2.7 Hz, 1H), 1.68 – 1.36 (m, 4H), 1.23 (td, J = 7.1, 2.6 Hz, 6H), 1.05 (s, 3H), 0.76 (s, 3H).

**¹³C NMR** (151 MHz, CDCl₃) δ 173.28, 173.05, 135.59, 123.53, 123.53, 61.48, 61.43, 57.24, 55.63, 48.93, 41.99, 37.02, 29.48, 29.43, 25.55, 23.83, 23.26, 22.75, 14.19.

GC (GC/MSD; HP-5MS UI; 139 KPα; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min): tR = 9.625 min. m/z calcd for C₁₉H₂₀O₄ (M)⁺ 322.2144

**MS** (EI, 70 eV): m/z (%) 322.3 (17), 277.3 (26), 276.3 (24), 249.3 (19), 203.2 (20), 192.2 (18), 174.2 (16), 173.1 (47), 135.1 (12), 122.1 (71), 105.1 (14), 93.1 (19), 79.1 (26)
(E)-diethyl 2-(3,7-dimethylocta-2,6-dienyl)-2-(2-methylallyl)malonate (SI 5)
The title compound was prepared by a previously reported procedure and the spectral data obtained matched those previously reported.
Godeau, J.; Olivero, S.; Antoniotti, S.; Dunach, E. Org. Lett. 2011, 13, 3320-3323.

(E)-diethyl 3,3-dimethyl-4-(6-methylhepta-2,5-dien-2-yl)cyclopentane-1,1-dicarboxylate (8)
Using general procedure A with the following modifications gave the title compound (44.6 mg, 0.127 mmol) as a clear yellow oil in 89% yield.
-temperature: rt
-salenCoCl: 3 mol% (2.81 mg, 0.00428 mmol)
-PhSiH₃: 6 mol% (1.05 μL, 0.00856 mmol)

¹H NMR (600 MHz, Chloroform-d) δ 5.21 – 5.01 (m, 2H), 4.31 – 3.99 (m, 4H), 2.70 (t, J = 7.5 Hz, 2H), 2.51 – 2.44 (m, 1H), 2.24 (qd, J = 6.5, 4.0 Hz, 2H), 2.21 – 2.10 (m, 2H), 1.68 (s, 3H), 1.63 (s, 2H), 1.30 – 1.16 (m, 6H), 1.05 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 173.25, 173.05, 132.65, 131.63, 126.20, 123.30, 61.49, 61.45, 57.22, 56.74, 48.81, 42.10, 37.24, 29.27, 27.22, 25.81, 23.84, 17.87, 16.89, 14.19, 14.17.

GC (GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C; then hold 2 min): tR = 9.957 min.

m/z calcd for C₂₀H₃₄O₄ (M)⁺ 336.2301

MS (EI, 70 eV): m/z (%) 336.3 (1), 237.2 (25), 167.2 (19), 163.2 (28), 122.1 (56), 121.1 (22), 109.1 (100), 107.1 (19), 93.1 (25), 91.1 (20), 82.1 (34)

Diethyl 2-(cyclohex-2-enyl)-2-(2-methylallyl)malonate (SI 6)
In a flame dried round bottom flask charged with sodium hydride (1.05 eq) was added THF (0.2M) under argon atmosphere. Diethyl 2-(2-methylallyl)malonate (1 eq.) in THF was added to this suspension at 0 °C and the mixture was stirred during 30 minutes. Bromo-2-cyclohexene (1.1 eq) was finally added and the reaction was stirred until completion. The reaction was quenched with water and worked-up with an aqueous solution of NaHCO₃ sat. and Et₂O. The organic phase was dried over magnesium sulfate, filtered and evaporated off. The crude residue was purified by flash chromatography on a short silica gel column with 3% Et₂O:hexane to furnish a clear oil in 89%.

¹H NMR (600 MHz, Chloroform-d) δ 5.82 – 5.73 (m, 1H), 5.69 (dddd, J = 12.6, 4.9, 2.9, 1.6 Hz, 1H), 4.80 (s 1H), 4.71 (s, 1H), 4.30 – 4.00 (m, 4H), 2.92 (ddt, J = 11.3, 4.8, 2.2 Hz, 1H), 2.84 – 2.55 (m, 2H), 1.96 – 1.89 (m, 2H), 1.89 – 1.83 (m, 1H), 1.77 (ddq, J = 13.3, 5.0, 2.4 Hz, 1H), 1.73 – 1.67 (m, 3H), 1.52 (tddt, J = 13.2, 10.5, 6.1, 2.8 Hz, 1H), 1.39 – 1.27 (m, 1H), 1.24 (dt, J = 11.3, 7.1 Hz, 6H).
\[^{13}\text{C}\ NMR\ (151\ MHz,\ CDCl}_3\ \delta\ 171.00,\ 170.63,\ 141.91,\ 128.48,\ 128.34,\ 115.03,\ 61.16,\ 60.98,\ 60.94,\ 40.87,\ 40.46,\ 25.15,\ 24.55,\ 23.80,\ 22.57,\ 14.24,\ 14.19\]

GC (GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min): \(t_R = 8.469\) min.

\[^{13}\text{C}\ NMR\ (151\ MHz,\ CDCl}_3\ \delta\ 172.80,\ 170.44,\ 126.65,\ 126.31,\ 63.17,\ 39.66,\ 32.20,\ 29.50,\ 25.15,\ 24.55,\ 23.80,\ 22.57,\ 14.25,\ 14.15\]

\[^{13}\text{C}\ NMR\ (151\ MHz,\ CDCl}_3\ \delta\ 172.80,\ 170.44,\ 126.65,\ 126.31,\ 63.17,\ 61.32,\ 61.22,\ 48.20,\ 47.15,\ 44.43,\ 39.66,\ 32.20,\ 29.50,\ 25.15,\ 24.55,\ 21.80,\ 14.25,\ 14.15\]

\[^{13}\text{C}\ NMR\ (151\ MHz,\ CDCl}_3\ \delta\ 172.80,\ 170.44,\ 126.65,\ 126.31,\ 63.17,\ 61.32,\ 61.22,\ 48.20,\ 47.15,\ 44.43,\ 39.66,\ 32.20,\ 29.50,\ 25.15,\ 24.55,\ 21.80,\ 14.25,\ 14.15\]

\[^{13}\text{C}\ NMR\ (151\ MHz,\ CDCl}_3\ \delta\ 172.80,\ 170.44,\ 126.65,\ 126.31,\ 63.17,\ 61.32,\ 61.22,\ 48.20,\ 47.15,\ 44.43,\ 39.66,\ 32.20,\ 29.50,\ 25.15,\ 24.55,\ 21.80,\ 14.25,\ 14.15\]

\[^{13}\text{C}\ NMR\ (151\ MHz,\ CDCl}_3\ \delta\ 172.80,\ 170.44,\ 126.65,\ 126.31,\ 63.17,\ 61.32,\ 61.22,\ 48.20,\ 47.15,\ 44.43,\ 39.66,\ 32.20,\ 29.50,\ 25.15,\ 24.55,\ 21.80,\ 14.25,\ 14.15\]

\[^{13}\text{C}\ NMR\ (151\ MHz,\ CDCl}_3\ \delta\ 172.80,\ 170.44,\ 126.65,\ 126.31,\ 63.17,\ 61.32,\ 61.22,\ 48.20,\ 47.15,\ 44.43,\ 39.66,\ 32.20,\ 29.50,\ 25.15,\ 24.55,\ 21.80,\ 14.25,\ 14.15\]
**1H NMR** (600 MHz, Chloroform-\(d\)) δ 5.00 – 4.88 (m, 1H), 4.79 (s, 1H), 4.69 (s, 1H), 4.14 (tdd, \(J\) = 12.2, 10.0, 5.7 Hz, 4H), 3.21 – 2.84 (m, 1H), 2.84 – 2.53 (m, 2H), 2.03 – 1.93 (m, 1H), 1.93 – 1.84 (m, 1H), 1.84 – 1.74 (m, 2H), 1.70 (d, \(J\) = 4.1 Hz, 3H), 1.56 – 1.48 (m, 1H), 1.24 (tdd, \(J\) = 11.1, 7.8, 4.4 Hz, 7H), 0.98 – 0.80 (m, 9H), 0.13 (s, 3H), 0.11 (s, 3H)

**13C NMR** (151 MHz, CDCl\(_3\)) δ 170.93, 170.08, 152.07, 142.11, 114.89, 105.34, 61.46, 60.91, 40.89, 40.40, 29.84, 25.83, 24.43, 23.87, 22.54, 18.11, 14.21, -4.13, -4.20

**GC (GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min):** \(t_R = 10.603\) min.

**m/z calcd for C\(_{23}\)H\(_{40}\)O\(_5\)Si (M)** \(+424.2645\)

**MS (EI, 70 eV):** \(m/z (\%) 424.3 (1), 211.2 (86), 210.2 (25), 153.1 (41), 151.1 (11), 141.1 (27), 123.1 (25), 122.1 (23), 96.1 (23), 95.1 (38), 75.1 (72), 68.1 (33)\)

**diethyl 4-(tert-butyldimethylsilyloxy)-3,3-dimethyl-3,3a,7,7a-tetrahydro-1H-indene-1,1(2H,6H)-dicarboxylate (10)**

Using general procedure A with the following modifications gave the title compound (44.2 mg, 0.104 mmol) as white brownish solid as a sole diastereoisomer in 88% yield. (silica gel column was neutralized with Et\(_3\)N)

- temperature: 60 °C
- salenCoCl: 3 mol% (2.33 mg, 0.00355 mmol)
- PhSiH\(_3\): 6 mol% (0.90 \(\mu\)L, 0.00710 mmol)

**1H NMR** (600 MHz, Chloroform-\(d\)) δ 4.79 (dd, \(J\) = 4.8, 3.1 Hz, 1H), 4.21 (dq, \(J\) = 6.9, 3.8 Hz, 3H), 4.15 - 4.09 (m, 1H), 3.02 – 2.70 (m, 1H), 2.53 (d, \(J\) = 14.3 Hz, 1H), 2.51 – 2.46 (m, 1H), 2.18 – 1.95 (m, 3H), 1.29 – 1.17 (m, 8H), 1.09 (s, 3H), 1.06 (s, 3H), 0.91 (s, 9H), 0.15 (s, 6H).

**13C NMR** (151 MHz, CDCl\(_3\)) δ 172.59, 170.21, 150.74, 102.20, 63.37, 61.35, 61.29, 51.97, 46.95, 45.79, 39.21, 33.77, 28.54, 25.93, 23.34, 21.49, 18.04, 14.29, 14.21, -4.29, -4.14

**GC (GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min):** \(t_R = 10.826\) min.

**m/z calcd for C\(_{23}\)H\(_{40}\)O\(_5\)Si (M)** \(+424.2645\)

**MS (EI, 70 eV):** \(m/z (\%) 424.4 (24), 379.4 (27), 367.2 (28), 351.3 (36), 350.3 (100), 335.3 (18), 249.2 (44), 247.2 (17), 151.1 (19), 145.1 (42), 123.1 (18), 122.1 (22), 75.1 (87)\)

**diethyl 2-benzyl-2-(2-methylallyl)malonate (SI 8)**

In a flame dried round bottom flask charged with sodium hydride (1.05 eq) was added some THF under argon atmosphere. Diethyl 2-(2-methylallyl)malonate (1 eq.) in THF was added to this suspension at 0 °C and the mixture was stirred during 30 minutes. Benzyl bromide (1.1 eq) was finally added and the reaction was stirred until completion. The reaction was quenched with water and worked-up with an aqueous solution of NaHCO\(_3\) sat. and Et\(_2\)O. The organic phase was dried over magnesium sulfate, filtered and evaporated off. The crude residue was purified by flash chromatography on a short silica gel column with 3 % Et\(_2\)O:hexane to furnish a clear oil in 89%.
\[ \text{H NMR (400 MHz, Chloroform-d)} \delta 7.29 - 7.19 (m, 3H), 7.13 (dt, J = 5.6, 1.8 Hz, 2H), 4.92 (s, 1H), 4.81 (s, 1H), 4.14 (qqd, J = 7.0, 3.7, 2.0 Hz, 4H), 3.30 (d, J = 2.0 Hz, 2H), 2.70 - 2.46 (m, 2H), 1.72 (s, 3H), 1.21 (td, J = 7.2, 1.9 Hz, 6H) \]

\[ \text{13C NMR (151 MHz, CDCl}_3\] \delta 171.33, 141.19, 136.61, 130.22, 128.23, 126.95, 115.10, 61.38, 58.53, 40.35, 38.76, 23.92, 14.07

GC (GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min): \( t_R = 8.904 \) min.

m/z calcd for \( \text{C}_{18}\text{H}_{24}\text{O}_4\) (M)\(^+\) 304.1675

MS (EI, 70 eV): m/z (%) 304.2 (2), 231.2 (63), 213.1 (49), 204.1 (17), 203.1 (100), 185.1 (35), 167.1 (77), 158.1 (34), 157.1 (63), 139.0 (23), 130.0 (20), 129.1 (27), 115.1 (28)

diethyl 4,4-dimethyl-3,4-dihyronaphthalen-2,2(1H)-dicarboxylate (11)

Using general procedure A with the following modifications gave the title compound (46.1 mg, 0.151 mmol) as a clear yellow oil in 92\% yield.

- temperature: rt
- salenCoCl: 3 mol\% (3.24 mg 0.00493 mmol)
- PhSiH\(_3\): 6 mol\% (1.20 \( \mu \)L, 0.00985 mmol)

Spectral information obtained matched those previously reported

Cacciuttolo, B.; Poulain-Martini, S.; Dunach, E.. Eur. J. Org. Chem. 2011, 20, 3710-3714

6-benzyl-3-ethoxycyclohex-2-enone

The title compound was prepared by a previously reported procedure, highlighted in the Scheme above and the spectral data obtained matched those previously reported.

Chen, Y.; Lee, C. J. Am. Chem. Soc. 2006, 128, 15598-15599
4-benzyl-3-methyl-4-(2-methylallyl)cyclohex-2-eneone (SI 9)

A solution of n-BuLi (2.4 M in hexanes, 1.05 eq) was added slowly to freshly distilled diisopropylamine (1.1 eq) in THF at −78°C and the solution was stirred for 30 min at -78°C and 15 min at 0°C and then cooled to -78°C. A solution of 6-benzyl-3-ethoxycyclohex-2-eneone (1 eq) in THF was added via cannula at -78°C and the solution was stirred for 60 min to obtain a slurry. 3-bromo-2-methylpropene (1 eq) was added in one portion, the mixture was stirred 1h at -78°C and 3h at r.t. The solution was then cooled to -78°C and MeLi (1.5 M in Et2O, 13.21 mL, 19.82 mmol) was added in one portion. The resulting mixture was stirred for 30 min at -78°C. It was then warmed to r.t. and the mixture stirred for 1h. A solution of HCl (1M, 30 mL) was added and the mixture stirred vigorously for 1h. Water (30 ml) was added with brine (30 mL) and Et₂O (30 mL) and the organic phases was separated. The aqueous layer was extracted with ethyl acetate (3x), and the combined organic phases were dried over MgSO₄, filtered and concentrated. The crude residue was purified by flash chromatography on a short silica gel column with 7-15 % Et₂O: hexane to furnish a clear yellow oil in 63%.

¹H NMR (400 MHz, Chloroform-δ) δ 7.27 (dddd, J = 14.4, 7.3, 3.7, 1.8 Hz, 3H), 7.14 (dt, J = 5.4, 1.7 Hz, 2H), 6.11 – 5.82 (m, 1H), 4.85 (q, J = 3.8, 2.9 Hz, 1H), 4.69 (d, J = 5.6 Hz, 1H), 3.06 – 2.87 (m, 1H), 2.87 – 2.70 (m, 1H), 2.49 (dd, J = 15.5, 5.5 Hz, 1H), 2.42 – 2.24 (m, 2H), 2.22 – 2.06 (m, 2H), 2.02 (d, J = 2.1 Hz, 3H), 1.78 (ddt, J = 5.7, 3.4, 2.0 Hz, 1H), 1.72 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 199.07, 167.10, 141.72, 137.14, 130.48, 129.22, 128.37, 126.91, 114.63, 44.70, 44.36, 42.92, 34.30, 29.55, 24.91, 21.07

GC (GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min): tR = 10.117 min.

m/z calcd for C₁₈H₂₀O (M)⁺ 254.1621

MS (EI, 70 eV): m/z (%) 254.2 (25), 129.1 (10), 128.1 (10), 105.1 (10), 93.1 (12), 92.1 (10), 91.1 (100), 65.1 (10)

2,4',4'-trimethyl-3',4'-dihydro-1'H-spiro[cyclohex[2]ene-1,2'-naphthalen]-4-one (12a)

Using general procedure A with the following modifications gave the title compound as a clear yellow oil in 42 % yield (21.3 mg, 0.101 mmol) at rt and 58% (28.9 mg, 0.120 mmol) at 100 °C.

-salenCoCl: 5 mol% (6.82 mg 0.0103 mmol)
-PhSiH₃: 10 mol% (2.54 μL, 0.0206 mmol)

¹H NMR (600 MHz, Chloroform-δ) δ 7.38 (dd, J = 7.8, 1.3 Hz, 1H), 7.29 – 7.21 (m, 2H), 7.15 (td, J = 7.4, 1.4 Hz, 1H), 7.12 – 7.02 (m, 1H), 5.90 (q, J = 1.3 Hz, 1H), 3.13 (d, J = 15.4 Hz, 1H), 2.62 (dd, J = 15.4, 2.5 Hz, 1H), 2.51 – 2.37 (m, 2H), 2.04 – 1.95 (m, 4H), 1.91 – 1.73 (m, 3H), 1.43 (s, 3H), 1.36 (s, 3H)
**13C NMR** (151 MHz, CDCl₃) δ 199.26, 168.62, 143.99, 134.22, 129.17, 127.83, 126.99, 126.09, 45.03, 39.31, 39.05, 35.07, 34.17, 33.94, 20.73.

**GC (GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min): tR = 10.254 min.**

**MS (EI, 70 eV): m/z calcd for C₁₈H₂₀O (M)⁺ 254.1621**

Using general procedure A with the following modifications gave the title compound as a clear yellow oil in 56 % yield (28.3 mg, 0.118 mmol) at rt and 41% (20.6 mg, 0.097 mmol) at 100 °C.

-salenCoCl: 5 mol% (6.82 mg 0.0103 mmol)
-PhSiH₃: 10 mol% (2.54 μL, 0.0206 mmol)

**1H NMR** (600 MHz, Chloroform-d) δ 7.25 (s, 1H), 7.17 (t, J = 7.4 Hz, 1H), 7.12 (t, J = 7.5 Hz, 1H), 7.03 (d, J = 7.4 Hz, 1H), 5.70 (s, 1H), 3.73 – 3.51 (m, 1H), 2.85 (d, J = 17.1 Hz, 1H), 2.79 – 2.66 (m, 1H), 2.51 (dt, J = 13.1, 2.7 Hz, 1H), 2.03 – 1.93 (m, 1H), 1.90 (dd, J = 14.3, 4.8 Hz, 1H), 1.71 (dt, J = 12.5, 6.5 Hz, 1H), 1.40 (dd, J = 14.3, 6.1 Hz, 1H), 1.04 (d, J = 6.6 Hz, 3H), 1.00 (d, J = 6.7 Hz, 3H).

**13C NMR** (101MHz, CDCl₃) δ 199.96, 164.91, 134.64, 133.48, 129.55, 129.06, 127.57, 126.49, 126.38, 49.36, 47.90, 38.83, 35.05, 25.82, 24.73, 24.36, 20.34

**GC (GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min): tR = 10.105 min.**

**MS (EI, 70 eV): m/z (%) 254.2 (81), 211.2 (41), 198.1 (37), 197.1 (100), 183.2 (69), 179.1 (83), 169.2 (24), 155.1 (27), 153.1 (32), 152.1 (26), 141.1 (46), 69.1 (26)**

3-methyl-6-(2-methylallyl)-6-(3-methylbut-2-enyl)cyclohex-2-enone (SI 10)

A solution of n-BuLi (2.4 M in hexanes,1.05 eq) was added slowly to freshly distilled diisopropylamine (1.1 eq) in THF at −78°C and the solution was stirred for 30 min at −78°C and 15 min at 0°C and then cooled to -78°C. A solution 3-methyl-6-(2-methylallyl)cyclohex-2-enone (1 eq) in THF was added via cannula at −78°C and the solution was stirred for 60 min to obtain a slurry. 3-3-dimethylallylbromide (1 eq) was added in one portion, the mixture was stirred 1h at -78°C and 3h at r.t. The reaction was quenched with water and worked-up with an aqueous solution of NH₄Cl sat. and Et₂O. The organic phase was dried over magnesium sulfate, filtered
and evaporated off. The crude residue was purified by flash chromatography on a short silica gel column with 3% Et₂O: hexane to furnish a clear oil in 75%.

**¹H NMR**: (400 MHz, Chloroform-d) δ 5.81 (s, 1H), 5.07 (dddt, J = 8.3, 6.8, 3.1, 1.5 Hz, 1H), 4.79 (dt, J = 2.8, 1.5 Hz, 1H), 4.64 (dd, J = 2.4, 1.3 Hz, 1H), 2.59 (dd, J = 13.7, 1.5 Hz, 1H), 2.34 – 2.25 (m, 2H), 2.25 – 2.18 (m, 1H), 2.10 (dd, J = 14.7, 8.2 Hz, 1H), 2.03 (dd, J = 13.6, 1.5 Hz, 1H), 1.91 (q, J = 1.1 Hz, 3H), 1.82 (dddd, J = 16.3, 12.5, 7.9, 6.1 Hz, 2H), 1.69 (s, 3H), 1.61 (s, 3H), 1.57 (s, 3H).

**¹³C NMR**: (151 MHz, CDCl₃) δ 202.89, 160.34, 142.95, 134.40, 126.09, 119.64, 114.79, 47.14, 42.46, 34.22, 29.75, 28.33, 26.19, 24.60, 24.20, 18.13

GC (GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min): tR = 7.908 min.

**m/z calcd for C₁₅H₂₀O (M)** + 232.1827

**MS** (EI, 70 eV): m/z (%) 232.2 (5), 177.1 (57), 174.2 (50), 163.1 (28), 161.1 (100), 159.1 (32), 123.1 (29), 121.1 (58), 109.1 (32), 107.1 (44), 105.1 (28), 95.1 (28), 93.1 (29), 91.1 (49), 82.1 (54)

2,2,8-trimethyl-3-(prop-1-en-2-yl)spiro[4.5]dec-7-en-6-one (13)

Using general procedure A with the following modifications gave the title compound (42.9 mg, 0.185 mmol) as a clear yellow oil in 86% yield and as a mixture of diastereomers (1:1.35) -temperature: rt -salenCoCl: 3 mol% (4.24 mg, 0.00646 mmol)

**¹H NMR**: (600 MHz, Chloroform-d) δ 5.82 (s, 1H), 5.75 (s, 1H), 4.86 (s, 1H), 4.83 (s, 1H), 4.72 (dt, J = 2.0, 1.0 Hz, 1H), 4.64 (dt, J = 2.2, 1.0 Hz, 1H), 2.46 (t, J = 13.1 Hz, 1H), 2.43 – 2.38 (m, 1H), 2.36 – 2.31 (m, 2H), 2.31 – 2.20 (m, 3H), 2.14 (d, J = 13.4 Hz, 1H), 2.05 – 1.93 (m, 3H), 1.93 – 1.85 (m, 8H), 1.78 – 1.75 (m, 3H), 1.75 – 1.70 (m, 3H), 1.49 (dd, J = 12.7, 6.0 Hz, 1H), 1.46 – 1.39 (m, 1H), 1.32 (d, J = 13.4 Hz, 1H), 1.11 (s, 3H), 1.07 (s, 3H), 0.84 (d, J = 2.8 Hz, 6H).

**¹³C NMR**: (151 MHz, CDCl₃) δ 203.76, 203.07, 160.32, 160.24, 144.87, 144.67, 125.94, 125.00, 112.28, 111.72, 55.19, 54.52, 50.35, 49.18, 48.29, 48.05, 42.17, 41.78, 39.56, 37.11, 37.08, 35.89, 30.41, 29.49, 29.42, 28.68, 24.95, 24.14, 24.08, 23.95, 23.80, 23.71

GC (GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min): tR = 8.074 min and 8.160 min.

m/z calcd for C₁₅H₂₀O (M)⁺ 232.1827

**MS** (EI, 70 eV): m/z (%) 232.2 (11), 176.1 (17), 174.2 (25), 164.2 (100), 163.2 (25), 161.1 (21), 123.1 (31), 109.1 (21), 108.1 (16), 107.1 (16), 82.1 (56), 79.1 (19), 77.1 (17)

**MS** (EI, 70 eV): m/z (%) 232.2 (3), 124.1 (9), 123.1 (100), 95.1 (11), 82.1 (14), 79.1 (9)
3-(2-methylallyloxy)cyclohex-1-ene (SI 11)

In a flame dried round bottom flask charged with sodium hydride (1.05 eq) was added some DMF under argon atmosphere. Cyclohexenol (1 eq.) in DMF was added to this suspension at 0 °C and the mixture was stirred during 30 minutes. 3-bromo-2-methylpropene (1.1 eq) was finally added and the reaction was stirred until completion of the reaction. The reaction was quenched with water and worked-up with an aqueous solution of NaHCO₃ sat. and Et₂O. The organic phase was dried over magnesium sulfate, filtered and evaporated off. The crude residue was purified by flash chromatography on a short silica gel column with 3% Et₂O: hexane to furnish a clear oil in 94%.

^1H NMR (600 MHz, Chloroform-d) δ 4.96 (s, 1H), 4.85 (s, 1H), 3.90 (s, 2H), 3.25 (tt, J = 9.3, 3.8 Hz, 1H), 2.07 – 1.80 (m, 2H), 1.73 (m, 3H), 1.63 – 1.41 (m, 1H), 1.39 – 1.09 (m, 5H).

^13C NMR (151 MHz, CDCl₃) δ 143.05, 130.88, 128.01, 111.89, 172.19, 172.06, 28.50, 25.37, 19.74, 19.41

GC (GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min): tR = 4.006 min.

m/z calcd for C₁₀H₁₆O (M)⁺ 152.1201

MS (EI, 70 eV): m/z (%) 152.1 (1), 109.1 (11), 108.1 (16), 82.1 (12), 81.1 (100), 80.1 (26), 79.1 (67), 69.1 (33), 68.1 (15), 67.1 (13)

3,3-dimethyl-2,3a,6,7,7a-hexahydrobenzofuran (14)

Using general procedure A with the following modifications gave the title compound (41.1 mg, 0.270 mmol) as a clear yellow oil in 82% yield.

-temperature: rt
-salenCoCl: 3 mol% (6.63 mg 0.0101mmol)
-PhSiH₃: 6 mol% (2.50 μL, 0.0202 mmol)

^1H NMR (600 MHz, Chloroform-d) δ 5.88 (ddt, J = 10.3, 5.1, 2.6 Hz, 1H), 5.59 (ddt, J = 11.0, 3.3, 1.3 Hz, 1H), 4.40 (td, J = 6.1, 3.1 Hz, 1H), 3.56 – 3.07 (m, 2H), 2.25 (ddq, J = 6.4, 4.6, 2.0 Hz, 1H), 2.07 (ddtt, J = 15.9, 8.5, 4.3, 2.2 Hz, 1H), 1.98 – 1.75 (m, 2H), 1.75 – 1.44 (m, 1H), 1.14 (s, 3H), 0.98 (s, 3H).

^13C NMR (151 MHz, CDCl₃) δ 129.13, 125.90, 79.38, 76.66, 47.89, 42.61, 27.42, 27.11, 22.30, 20.25

GC (GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min): tR = 4.063 min.

m/z calcd for C₁₀H₁₆O (M)⁺ 152.1201

MS (EI, 70 eV): m/z (%) 152.1 (5), 121.1 (15), 81.1(14), 80.1 (100), 79.1 (59), 78.1 (16), 77.1 (16), 56.1 (16)
3-methyl-1-(2-methylallyloxy)but-2-ene (SI 12)
The title compound was prepared by a previously reported procedure and the spectral data obtained matched those previously reported.
Tokuyasu, T.; Kunikawa, S.; McCullough, K. J.; Masuyama, A.; Nojima, M. J. Org. Chem. 2005, 70, 251-260

3,3-dimethyl-4-(prop-1-en-2-yl)tetrahydrofuran (16)
Using general procedure A with the following modifications gave the title compound (41.1 mg, 0.293 mmol) as a clear yellow oil in 82 % yield.
-temperature: rt
-salenCoCl: 3 mol% (7.03 mg 0.0107mmol)
-PhSiH$_3$: 6 mol% (2.60 μL, 0.0214 mmol)
$^1$H NMR (600 MHz, Chloroform-δ) δ 4.90 (s, 1H), 4.71 (s, 1H), 4.03 (dd, $J = 8.6, 7.6$ Hz, 1H), 3.90 (t, $J = 8.4$ Hz, 1H), 3.71 – 3.49 (m, 2H), 2.46 (td, $J = 7.9, 1.0$ Hz, 1H), 1.77 (dd, $J = 1.5, 0.8$ Hz, 3H), 1.13 (s, 3H), 0.93 (s, 3H).
$^{13}$C NMR (151 MHz, CDCl$_3$) δ 143.20, 112.64, 81.29, 71.63, 55.78, 41.90, 26.94, 23.81, 21.60.
GC (GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min): tR = 7.325 min and 7.491 min. m/z calcd for C$_9$H$_{16}$O (M)$^+$ 140.1201
MS (EI, 70 eV): m/z (%) 140.0 (1), 93.1 (43), 79.1 (8), 72.1 (45), 69.1 (19), 68.1 (100), 67.1 (79), 53.1 (18)

(2-methyl-1-(3-methylbut-2-enyloxy)allyl)benzene (SI 13)
In a flame dried round bottom flask charged with sodium hydride (1.05 eq) was added some DMF under argon atmosphere. 2-methyl-1-phenylprop-2-en-1-ol (1 eq.) in DMF was added to this suspension at 0 °C and the mixture was stirred during 30 minutes. 3,3-dimethylallyl bromide(1.1 eq) was finally added and the reaction was stirred until completion of the reaction. The reaction was quenched with water and worked-up with an aqueous solution of NaHCO$_3$ sat. and Et$_2$O. The organic phase was dried over magnesium sulfate, filtered and evaporated off. The crude residue was purified by flash chromatography on a short silica gel column with 3% Et$_2$O:hexane to furnish a clear oil in 91%.
$^1$H NMR (600 MHz, Chloroform-δ) δ 7.43 – 7.38 (m, 2H), 7.35 (dd, $J = 8.5, 6.8$ Hz, 2H), 7.30 – 7.19 (m, 1H), 5.44 (tdt, $J = 5.6, 2.8, 1.4$ Hz, 1H), 5.14 (s, 1H), 5.00 (s, 1H), 4.79 (s, 1H), 4.03
(ddt, $J = 11.9, 7.0, 1.0$ Hz, 1H), 3.96 (dd, $J = 11.7, 6.9$ Hz, 1H), 1.78 (s, 3H), 1.66 (s, 3H), 1.63 (s, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 145.43, 140.91, 136.66, 128.18, 127.31, 126.80, 121.50, 113.02, 84.32, 65.15, 25.93, 18.19, 17.86

GC (GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min): $t_R = 6.655$ min.

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 145.43, 140.91, 136.66, 128.18, 127.31, 126.80, 121.50, 113.02, 84.32, 65.15, 25.93, 18.19, 17.86

GC (GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min): $t_R = 7.325$ min and 7.491 min.

$m/z$ calcd for C$_{15}$H$_{20}$O (M)$^+$ 216.1514

MS (El, 70 eV): $m/z$ (%) 216.2 (1), 182.2 (10), 147.1 (30), 117.1 (31), 116.1 (18), 115.1 (30), 105.1 (25), 91.1 (44), 83.1 (12), 69.1 (57)

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 144.78, 142.57, 140.35, 139.22, 127.90, 127.42, 127.27, 126.78, 126.62, 113.64, 112.90, 90.66, 88.98, 71.23, 69.15, 56.46, 56.27, 45.14, 44.95, 25.64, 24.54, 24.22, 23.98, 22.47, 17.17.

GC (GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min): $t_R = 7.325$ min and 7.491 min.

$m/z$ calcd for C$_{15}$H$_{20}$O (M)$^+$ 216.1514

MS (El, 70 eV): $m/z$ (%) 216.2 (1), 182.2 (10), 110.1 (16), 105.1 (25), 91.1 (44), 83.1 (12), 67.1 (14)

MS (El, 70 eV): $m/z$ (%) 216.2 (1), 148.1 (27), 105.1 (9), 91.1 (14), 77.1 (12), 67.1 (14)

(4-methyl-3-(3-methylbut-2-enyloxy)pent-4-enyl)benzene (SI 14)

In a flame dried round bottom flask charged with sodium hydride (1.05 eq) was added some DMF under argon atmosphere. 2-methyl-5-phenylpent-1-en-3-ol (1 eq.) in DMF was added to this suspension at 0 °C and the mixture was stirred during 30 minutes. 3,3-dimethylallyl bromide (1.1 eq) was finally added and the reaction was stirred until completion of the reaction. The reaction was quenched with water and worked-up with an aqueous solution of NaHCO$_3$ sat. and Et$_2$O. The organic phase was dried over magnesium sulfate, filtered and evaporated off. The crude residue was purified by flash chromatography on a short silica gel column with 3% Et$_2$O:hexane to furnish a clear oil in 91%.
1H NMR (600 MHz, Chloroform-d) δ 7.33 – 7.23 (m, 2H), 7.18 (ddt, J = 14.3, 6.8, 1.5 Hz, 3H), 5.37 (s, J = 7.0, 5.7, 1.4 Hz, 1H), 4.94 (dt, J = 2.9, 1.5 Hz, 1H), 4.89 (dt, J = 2.0, 0.9 Hz, 1H), 3.92 (ddt, J = 11.5, 6.9, 1.0 Hz, 1H), 2.71 (ddd, J = 13.9, 9.8, 5.7 Hz, 1H), 2.60 (ddd, J = 13.9, 9.7, 6.4 Hz, 1H), 1.96 (dddd, J = 13.6, 9.7, 7.9, 5.8 Hz, 1H), 1.79-1.75 (m, 1H), 1.76 (s, 3H), 1.68 (s, 3H), 1.66 (d, J = 0.9 Hz, 3H).

13C NMR (151 MHz, CDCl3) δ 145.09, 142.33, 136.90, 128.65, 128.42, 125.83, 121.52, 113.57, 82.63, 64.76, 35.53, 32.25, 26.01, 18.17, 16.78

GC (GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min): tR = 7.840 min.

m/z calcd for C17H24O (M) + 244.1827

MS (EI, 70 eV): m/z (%) 244.2 (4), 104.1 (31), 103.1 (19), 92.1 (23), 91.1 (75), 85.1 (16), 69.1 (100), 68.1 (10), 67.1 (11)

3,3-dimethyl-2-phenethyl-4-(prop-1-en-2-yl)tetrahydrofuran (18)

Using general procedure A with the following modifications gave the title compound (45.3 mg, 0.185 mmol) as a clear oil in 90% yield and as a mixture of diastereomers (1:2.32)

-temperature: rt
-salenCoCl: 3 mol% (4.03 mg, 0.00613 mmol)
-PhSiH3: 6 mol% (1.50 μL, 0.0123 mmol)

1H NMR (600 MHz, Chloroform-d) δ 7.59 – 6.90 (m, 5H), 4.91 (p, J = 1.6 Hz, 1H), 4.74 (dd, J = 1.7, 0.9 Hz, 1H), 4.71 (dd, J = 1.8, 0.9 Hz, 1H), 4.08 (dd, J = 8.9, 7.4 Hz, 1H), 4.02 – 3.85 (m, 1H), 3.81 (dd, J = 8.9, 6.2 Hz, 1H), 3.53 (dd, J = 10.3, 2.5 Hz, 1H), 3.51 – 3.47 (m, 1H), 3.06 – 2.79 (m, 2H), 2.62 (ddt, J = 13.4, 8.9, 6.5 Hz, 2H), 2.46 (ddd, J = 7.2, 6.1, 0.8 Hz, 1H), 1.75 – 1.50 (m, 4H), 1.00 (s, 1H), 0.98 (s, 2H), 0.88 (s, 2H), 0.73 (s, 1H).

13C NMR (151 MHz, CDCl3) δ 144.85, 142.73, 142.63, 141.69, 128.58, 128.46, 125.87, 113.30, 112.63, 88.19, 86.44, 70.40, 68.77, 56.75, 56.53, 43.59, 43.36, 33.90, 33.86, 32.99, 32.24, 24.61, 24.53, 24.12, 24.03, 22.04, 16.44.

GC (GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min): tR = 8.355 min and 8.5444 min. m/z calcd for C17H24O (M) + 244.1827

MS (EI, 70 eV): m/z (%) 244.2 (1), 177.2 (14), 176.2 (100), 105.1 (23), 104.1 (11), 69.1 (14), 68.1 (15), 67.1 (30), 65.0 (13), 55.1 (15)

MS (EI, 70 eV): m/z (%) 244.2 (1), 176.2 (52), 110.1 (11), 105.1 (12), 96.1 (10), 95.1 (100), 91.1 (40), 67.1 (16)
tert-butyl benzyl(2-methylallyl)carbamate
The title compound was prepared by a previously reported procedure and the spectral data obtained matched those previously reported.
Liu, P.; Huang, L.; Lu, Y.; Dilweghani, M.; Baum, J.; Xiang, T.; Adams, J.; Tasker, A.; Larsen, R; Faul, M. M. Tet. Lett. 2007, 48, 2307-2310.

N-benzyl-3-methyl-N-(2-methylallyl)but-2-en-1-amine (SI 15)
In a flame dried round bottom flask charged with cesium carbonate (1.05 eq) was added some DMF under argon atmosphere. N-benzyl-2-methylprop-2-en-1-amine( 1 eq.) in MeCN was added to this suspension at room temperature. 3,3-dimethylallyl bromide(1.1 eq) was finally added and the reaction was stirred until completion of the reaction. The reaction was quenched with water and worked-up with Et<sub>2</sub>O. The organic phase was dried over magnesium sulfate, filtered and evaporated off. The crude residue was purified by flash chromatography on a short silica gel column with 50-100 % Et<sub>2</sub>O: hexane to furnish a clear oil in 77%.

<sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 7.38 – 7.33 (m, 2H), 7.30 (tt, J = 8.0, 1.7 Hz, 2H), 7.27 – 7.19 (m, 1H), 5.27 (tdq, J = 7.0, 2.7, 1.4 Hz, 1H), 4.93 (s, 1H), 4.84 (s, 1H), 3.50 (s, 2H), 2.96 (dd, J = 6.5, 2.0 Hz, 2H), 2.92 (d, J = 2.0 Hz, 2H), 1.76 (s, 3H), 1.73 (s, 3H), 1.59 (s, 3H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 144.48, 140.39, 134.68, 126.84, 128.19, 126.69, 122.20, 112.43, 60.85, 57.98, 51.21, 26.06, 20.97, 18.18 GC (GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min): t<sub>R</sub> = 7.216 min.

m/z calcd for C<sub>16</sub>H<sub>23</sub>N (M)<sup>+</sup> 229.1830

MS (EI, 70 eV): m/z (%) 229.2 (5), 92.1 (9), 91.1 (100), 65.1 (9)

1-benzyl-3,3-dimethyl-4-(prop-1-en-2-yl)pyrrolidine (19)
Using general procedure A with the following modifications gave the title compound (40.5 mg, 0.177 mmol) as a clear yellow oil in 81% yield.
-temperature: 60 °C
-salenCoCl: 5 mol% (7.16 mg 0.0108 mmol)
-PhSiH<sub>3</sub>: 10mol% (2.70 μL, 0.0216 mmol)

<sup>1</sup>H NMR (600 MHz, Chloroform-d) δ 7.41 – 7.27 (m, 4H), 7.25 – 7.20 (m, 1H), 4.83 (s, 1H), 4.70 (s, 1H), 3.66 (d, J = 13.1 Hz, 1H), 3.56 (d, J = 12.9 Hz, 1H), 2.84 (dd, J = 9.3, 7.1 Hz, 1H), 2.61 (t, J = 8.4 Hz, 2H), 2.48 (dd, J = 9.4, 7.3 Hz, 1H), 2.25 (d, J = 9.1 Hz, 1H), 1.75 (t, J = 1.1 Hz, 3H), 1.16 (s, 3H), 0.89 (s, 3H).
\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 128.76, 128.31, 126.12, 111.54, 69.55, 60.43, 58.18, 55.14, 40.47, 30.38, 24.55, 24.10\)

GC (GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min): \(t_R = 7.456 \text{ min.}\)

\(m/z\) calcd for C\(_{16}\)H\(_{23}\)N (M)\(^+\) 229.1830

MS (EI, 70 eV): \(m/z\) (%) 229.2 (7), 173.2 (54), 172.2 (15), 132.1 (45), 91.1 (100), 65.1 (13)

1-(2-methylallyl)-2-phenyl-1H-imidazole (SI 16)

In a flame dried round bottom flask charged with sodium hydride (1.05 eq) was added some DMF under argon atmosphere. 2-phenylimidazole (1 eq.) in DMF was added to this suspension at 0 °C and the mixture was stirred during 30 minutes. 3-bromo-2-methylpropene (1.1 eq) was finally added and the reaction was stirred until completion of the reaction. The reaction was quenched with water and worked-up with an aqueous solution of NaHCO\(_3\) sat. and Et\(_2\)O. The organic phase was dried over magnesium sulfate, filtered and evaporated off. The crude residue was purified by flash chromatography on a short silica gel column with 50-100 % Et\(_2\)O: hexane to furnish a clear oil in 83%.

\(^1\)H NMR (400 MHz, Chloroform-d) \(\delta 7.67 – 7.51 (m, 2H), 7.51 – 7.32 (m, 3H), 7.15 (t, \(J = 1.0\) Hz, 1H), 6.97 (t, \(J = 1.0\) Hz, 1H), 4.99 (dd, \(J = 2.8, 1.5\) Hz, 1H), 4.69 (dq, \(J = 2.2, 1.0\) Hz, 1H), 4.48 (t, \(J = 1.6\) Hz, 2H), 1.71 (s, 3H)

\(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta 148.14, 141.29, 130.66, 128.88, 128.74, 128.71, 128.62, 121.42, 112.94, 52.51, 20.11\)

GC (GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min): \(t_R = 7.943 \text{ min.}\)

\(m/z\) calcd for C\(_{13}\)H\(_{14}\)N\(_2\) (M)\(^+\) 198.1157

MS (EI, 70 eV): \(m/z\) (%) 198.2 (100), 197.1 (39), 157.1 (63), 117.1 (39), 116.1 (16), 89.1 (22), 55.1 (20)

6,6-dimethyl-5,6-dihydroimidazo[2,1-a]isoquinoline (20)

Using general procedure A with the following modifications gave the title compound (50 mg, 0.25 mmol) as a clear yellow oil in 77% yield.

-temperature: 60 °C
-salenCoCl: 3mol% (4.92 mg, 0.0075 mmol) + 3 mol% (4.92 mg, 0.0075 mmol)
-PhSiH\(_3\): (1.85 \(\mu\)L, 0.0150 mmol)

\(^1\)H NMR (600 MHz, Chloroform-d) \(\delta 8.13 – 7.99 (m, 1H), 7.41 – 7.30 (m, 3H), 7.16 (d, \(J = 1.2\) Hz, 1H), 6.93 (d, \(J = 1.2\) Hz, 1H), 3.88 (s, 2H), 1.34 (s, 6H)

\(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta 143.97, 141.44, 129.05, 129.02, 127.44, 125.61, 124.09, 124.05, 119.33, 55.37, 35.53, 26.88\)

GC (GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min): \(t_R = 8.349 \text{ min.}\)
m/z calcd for C₁₅H₁₈N₂ (M)⁺ 198.1157

**MS (EI, 70 eV):** m/z (%) 198.2 (58), 184.13 (13), 183.1 (100), 182.2 (8), 168.1 (10)

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5-benzylbicyclo[4.1.0]heptan-2-one (SI 17)
The title compound was prepared by a previously reported procedure and the spectral data obtained matched those previously reported.

Fagnoni, M.; Schmoldt, P.; Kirschberg, T.; Mattay, J. *Tetrahedron*. 1998, 54, 6427-6444.

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2-benzyl-5-methylenebicyclo[4.1.0]heptane (21)
In a flame dried round bottom flask charged with methyltriphenylphosphonium bromide (1.05 eq) was added some THF under argon atmosphere and cooled down to 0 °C. KHMDS in toluene (0.5 M, 1.05 eq.) in toluene was added to this suspension at 0 °C and the mixture was stirred during 30 minutes. 5-benzylbicyclo[4.1.0]heptan-2-one (1 eq) was finally added and the reaction was stirred until completion of the reaction determined by TLC. The reaction was quenched with water and worked-up with an aqueous solution of NaHCO₃ sat. and Et₂O. The organic phase was dried over magnesium sulfate, filtered and evaporated off. The crude residue was purified by flash chromatography on a short silica gel column with 3% Et₂O:hexane to furnish a clear oil in 77%.

**¹H NMR** (400 MHz, Chloroform-d) δ 7.35 – 7.25 (m, 2H), 7.24 – 7.15 (m, 3H), 4.85 (s, 1H), 4.72 (s, 1H), 2.80 (ddt, J = 13.3, 7.6, 2.3 Hz, 1H), 2.68 (ddt, J = 13.4, 7.9, 2.3 Hz, 1H), 2.16 (ddt, J = 14.9, 6.0, 2.9 Hz, 1H), 2.02 (ddtq, J = 9.8, 7.4, 4.7, 2.3 Hz, 1H), 1.86 (ddtq, J = 15.3, 11.1, 4.1, 2.0 Hz, 1H), 1.63 (tdd, J = 8.0, 5.1, 2.3 Hz, 1H), 1.54 (tdd, J = 9.6, 5.6, 5.2, 2.6 Hz, 1H), 1.13 (tdd, J = 11.4, 9.2, 4.1, 1.9 Hz, 1H), 1.04 (dttd, J = 13.1, 8.0, 2.3 Hz, 1H), 0.83 (tdd, J = 9.0, 4.6, 2.4 Hz, 1H), 0.44 (qd, J = 5.1, 2.4 Hz, 1H)

**¹³C NMR** (151 MHz, CDCl₃) δ 147.91, 141.23, 129.17, 128.36, 125.94, 106.95, 43.40, 37.03, 30.22, 28.67, 19.08, 13.75

GC (GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min): tR = 7.462 min.

m/z calcd for C₁₅H₁₈N₂ (M)⁺ 198.1409
**MS** (El, 70 eV): m/z (%) 198.2 (9), 142.1 (53), 129.1 (19), 115.1 (16), 107.1 (47), 106.1 (14), 105.1 (12), 92.1 (19), 91.1 (100), 79.1 (62), 65.1 (20)

7-methyl-4b,5,8,9,9a,10-hexahydrobenzo[a]azulene (22)

Using general procedure A with the following modifications gave the title compound (23 mg, 0.116 mmol, racemic) as a clear yellow oil in 75% yield.

- temperature: 80 °C
- salenCoCl: 2 mol%
- PhSiH₃: 50 mol%

1H NMR (600 MHz, Chloroform-d) δ 7.09 (m, 4H), 5.32 (s, 1H), 2.88 – 2.78 (m, 2H), 2.61 – 2.44 (m, 2H), 2.20 – 2.06 (m, 2H), 2.02 – 1.95 (m, 1H), 1.90 – 1.83 (m, 1H), 1.71 (t, J = 1.6 Hz, 3H), 1.52 (tdd, J = 12.1, 9.8, 4.5, 2.4 Hz, 2H), 1.42 (qd, J = 12.1, 5.7 Hz, 1H).

13C NMR (151 MHz, CDCl₃) δ 137.34, 137.28, 134.61, 129.24, 129.10, 125.69, 125.59, 125.24, 77.37, 77.16, 76.95, 38.35, 37.15, 37.13, 36.83, 30.61, 29.84, 23.76.

GC (GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min): tR = 7.805 min.

m/z calcd for C₁₅H₁₈(M)⁺ 198.1409

**MS** (El, 70 eV): m/z (%) 198.2 (55), 143.1 (24), 142.1 (100), 141.1 (56), 129.1 (28), 128.1 (31), 115.1 (19), 91.1 (14)

**Complexes Molecules**

Humulene II epoxide ((1R,3E,7E,11R)-1,5,5,8-tetramethyl-12-oxabicyclo[9.1.0]dodeca-3,7-diene) (23)

To a flame dried 150 mL round bottom flask was added a stir bar, Co(III)salenCl (1 mol%, 31.3 mg.), (-)-caryophyllene oxide (22) (1.0 eq., 1.05 g., 4.77 mmol), and benzene (not dried) (48 mL, 0.1 M). The reaction was degassed with Argon for 20 minutes, followed by the addition of phenylsilane (2 mol%, 11.7 μL). The dark green solution turned a red-orange color and the reaction was monitored by GCMS. After completion at 5 hours, the reaction was concentrated directly in vacuo and purified by FCC on silica with 5% EtOAc/hex to obtain a pale yellow oil in 95% yield (1.0 g., 4.54 mmol).

1H NMR (600 MHz, Chloroform-d) δ 5.28 (ddd, J = 15.5, 10.1, 5.2 Hz, 1H), 5.15 (d, J = 15.8 Hz, 1H), 5.07-4.92 (m, 1H), 2.62-2.48 (m, 2H), 2.24 (m, 1H), 2.14 (m, 2H), 1.99 (dd, J = 13.7, 9.2 Hz, 1H), 1.92-1.81 (m, 1H), 1.68-1.60 (m, 1H), 1.35 (m, 1H), 1.30 (s, 3H), 1.11 (s, 3H), 1.08 (s, 3H).
\[^{13}\text{C}\] NMR (151 MHz, CDCl\(_3\)) \(\delta 143.25, 132.05, 125.86, 122.23, 77.37, 77.16, 76.95, 63.37, 62.09, 42.74, 40.37, 36.77, 36.66, 29.86, 24.90, 17.35, 15.24\).

GC (GC/MSD; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min): \(t_R = 7.365\) min.

\(m/z\) calcd for \(\text{C}_{15}\text{H}_{24}\text{O}\) (M)\(^+\) 220.1827

\(\text{MS}\) (EI, 70 eV): \(m/z\) (%): 220.2 (3), 147.2 (20), 138.1 (39), 123.1 (23), 121.1 (29), 110.2 (18), 109.2 (59), 107.1 (29), 105.1 (30), 96.1 (51), 94.1 (17), 93.1 (100), 92.1 (19), 91.1 (39), 82.1 (26), 81.1 (31), 80.1 (29), 79.0 (34), 77.1 (28), 69.1 (21), 68.1 (23), 67.1 (55), 55.1 (24), 53.1 (21)

[\(\alpha\)]\(_D\)\(^{20}\) @ 589 nm in CHCl\(_3\); c = 0.25, \(-110.4^\circ\) mL/dm.g.

\(\alpha\)-funebrene (25)

Using general procedure A with the following modifications gave the title compound, \(\alpha\)-funebrene (9 mg, 0.044 mmol) from \(\beta\)-Funebrene (24) as a clear colorless oil in 90% yield.
- temperature: rt
- salenCoCl: 2 mol%
- PhSiH\(_3\): 3 mol%

The spectral data obtained matched those previously reported. Paknikar, S.K.; Bhatwadekar, B.V.; Chakravarti, K.K., *Tetrahedron Lett.* 1975, 34, 2973 (corrects assignment from Kaiser R.; Naegeli P. *Tetrahedron Lett.* 1972, 20, 2009.)