Supporting Information

Synthesis of Highly Functionalized Tri-and Tetrasubstituted Alkenes via Pd-Catalyzed 1,2-Hydrovinylation of Terminal 1,3-Dienes

Vaneet Saini, Mark O’Dair, and Matthew S. Sigman*

Department of Chemistry, University of Utah, 315 South 1400 East, Salt Lake City, Utah 84112-0085, United States

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**General considerations:** Anhydrous dimethylacetamide (DMA) was purchased from Aldrich and dried over activated 3 Å molecular sieves. THF was passed through an alumina column (Innovative Technology®) solvent system. Anhydrous 1AmOH was used as purchased from Aldrich. Tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct was prepared according to the reported procedure. Cyclic enol nonaflates and triflates were prepared according to the literature procedures. Cyclic enol nonaflates and triflates were prepared according to the literature procedures unless otherwise mentioned. All other reagents were obtained from commercial sources and used without further purification. H NMR spectra were obtained at 300 MHz, 400 MHz or 500 MHz, chemical shifts are reported in ppm, and referenced to the CDCl$_3$ singlet at 7.26 ppm or CD$_2$Cl$_2$ at 5.32 ppm. C NMR spectra were obtained at 75 MHz, 100 MHz or 126 MHz and referenced to the center line of the CDCl$_3$ triplet at 77.23 ppm or CD$_2$Cl$_2$ quintet at 53.84 ppm. The abbreviations s, d, t, q, quint, sex, sep, dd, dt, td, m and br stand for the resonance multiplicities singlet, doublet, triplet, quartet, quintet, sextet, septet, doublet of doublets, doublet of triplets, triplet of doublets, multiplet and broad signal, respectively. Thin-layer chromatography was performed with EMD silica gel 60 F254 plates eluting with solvents indicated, visualized by a 254 nm UV lamp and stained with phosphomolybdic acid stain. Flash chromatography was performed using EM reagent silica 60 (230-400 mesh). IR spectra were recorded using a Thermo Nicolet FT-IR. High resolution mass spectrometry (HRMS) data were obtained on a Waters LCP Premier XE instrument by ESI/TOF.

**Preparation of Starting Materials:**

**Preparation of (E)-buta-1,3-dien-1-ylbenzene (1a):**

![diene 1a](attachment:diene_1a.png)

The diene 1a was prepared according to the literature procedure. Analytical data matches the literature.

**Preparation of 1-(buta-1,3-dien-1-yl)-4-methoxybenzene (1b):**

![benzene 1b](attachment:benzene_1b.png)
The diene 1b was prepared according to the literature procedure. Analytical data matches the literature.

**Preparation of 5-(buta-1,3-dien-1-yl)-2-methoxyphenol (1c):**

![Chemical structure of 1c]

To a 250 mL oven dried round bottom flask was added 9.6 g of allyltriphenylphosphonium bromide (2.5 equiv, 25 mmol). The flask was purged with N₂ and 100 mL of THF was added. The suspension was cooled to 0°C and 9.2 mL of a n-BuLi solution (2.5 M solution in hexanes, 23 mmol, 2.3 equiv) was added drop wise by syringe. The reaction mixture was stirred for 15 min followed by drop wise addition of 1.5 g of isovanillin (1.0 equiv, 10 mmol) in 15 mL THF. After 1 h, the reaction mixture was allowed to slowly warm to rt and stirred for 16 h. A saturated solution of NH₄Cl (50 ml) was added followed by extraction with Et₂O (2X50 ml). The combined organic phases were washed with brine, dried over MgSO₄ and solvents removed under reduced pressure. The product was then purified by flash column chromatography (10→20% Et₂O:hexanes) to afford 1c as a white solid (1.4 g, 80% yield, Z:E::2.4:1.0), Mp = 32 °C, Rf = 0.13 (5% EtOAc:hexanes). ¹H NMR (500 MHz, CDCl₃) reported as a mixture of isomers relative to 1H of Z isomer; δ 7.04 (d, J = 5.0 Hz, 0.38H), 6.95-6.87 (m, 2.24H), 6.82 (d, J = 1.5 Hz, 2H), 6.80 (d, J = 5.0 Hz, 0.40H), 6.66 (dd, J = 17.5, 12.5, 0.42H), 6.51-6.44 (m, 0.78H), 6.35 (d, J = 10.0 Hz, 1H), 6.18 (t, J = 10.0 Hz, 1H), 5.58 (s, 1H), 5.57 (s, 0.29H), 5.35 (d, J = 15.0 Hz, 1H), 5.29 (d, J = 15.0 Hz, 0.42H), 5.20 (d, J = 10.0 Hz, 1H), 5.12 (d, J = 10.0 Hz, 0.39H), 3.39 (s, 3H), 3.89 (s, 1.08H); ¹³C NMR (126 MHz, CDCl₃) δ 146.6, 146.0, 145.8, 145.4, 137.4, 133.5, 132.6, 131.1, 130.1, 129.9, 128.3, 121.4, 119.3, 119.2, 116.9, 115.3, 112.0, 110.8, 110.6, 56.1; ATR-FTIR (neat); 3510, 3010, 2935, 2839, 2360, 2342, 1506, 1439, 1264, 1227, 1210, 1128, 1025, 1002, 966, 905, 817, 762, 668. HRMS (ESI) m/z (M+H)⁺ calculated for C₁₁H₁₃O₂: 177.0916 observed: 177.0915.

**Preparation of 4-(buta-1,3-dien-1-yl)phenol (1d):**

![Chemical structure of 1d]

The same general procedure as that for the synthesis of 1c was followed using 1.2 g of p-hydroxybenzaldehyde (10 mmol, 1.0 equiv), 9.6 g of allyltriphenylphosphonium bromide (25 mmol, 2.5
equiv) and 9.2 mL of a n-BuLi solution (2.5 M solution in hexanes, 23 mmol, 2.3 equiv). The product was then purified by flash column chromatography (10→20% Et₂O:hexanes) to afford 1d as a yellow paste (1.40 g, 96% yield, Z:E::1.5:1.0), R_f = 0.33 (20% Et₂O:hexanes). ¹H NMR (500 MHz, CDCl₃) reported as a mixture of isomers relative to 1H of Z isomer; δ 7.31 (d, J = 5.0 Hz, 1.20H), 7.23 (d, J = 10.0 Hz, 2H), 6.92-6.85 (m, 1H), 6.82 (d, J = 10.0 Hz, 2H), 6.80 (d, J = 10.0 Hz, 1.18H), 6.67 (dd, J = 15.0, 10.0 Hz, 0.74H), 6.50 (td, J = 20.0, 7.5 Hz, 1.25H), 6.39 (d, J = 10.0 Hz, 1H), 6.20 (t, J = 10.0 Hz, 1H), 5.36 (d, J = 20.0 Hz, 1H), 5.30 (d, J =15.0 Hz, 0.65H), 5.21 (d, J = 10.0 Hz, 1H), 5.13 (d, J = 10.0 Hz, 0.67H), 5.08 (s, 0.58H), 5.07 (s, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 155.3, 154.7, 137.5, 133.4, 132.5, 130.7, 130.5, 130.4, 130.0, 129.7, 128.1, 128.0, 119.3, 116.8, 115.8, 115.4; ATR-FTIR (neat); 3350, 2989, 2870, 2360, 1608, 1509, 1445, 1377, 1240, 1172, 1143, 1001, 903, 846, 824. HRMS (ESI) m/z (M+H)⁺ calculated for C₁₀H₁₁O: 147.0810 observed: 147.0813.

Preparation of (E)-buta-1,3-dien-1-ylcyclohexane (1e):

\[
\text{\begin{tikzpicture}
\draw [-latex] (0,0) -- (1,0);
\draw [-latex] (1,0) -- (2,0);
\end{tikzpicture}}\]

The diene 1e was prepared according to the literature procedure.⁸ Analytical data matches the literature.⁸

Preparation of 4,4-dimethyl-1-vinylcyclohex-1-ene (1f):

\[
\text{\begin{tikzpicture}
\draw [-latex] (0,0) -- (1,0);
\draw [-latex] (1,0) -- (2,0);
\draw [-latex] (2,0) -- (3,0);
\draw [-latex] (3,0) -- (4,0);
\end{tikzpicture}}\]

The diene 1f was prepared according to the literature procedure.⁹ Analytical data matches the literature.⁹

Preparation of (E)-4,8-dimethylnona-1,3,7-triene (1g):

\[
\text{\begin{tikzpicture}
\draw [-latex] (0,0) -- (1,0);
\draw [-latex] (1,0) -- (2,0);
\draw [-latex] (2,0) -- (3,0);
\draw [-latex] (3,0) -- (4,0);
\draw [-latex] (4,0) -- (5,0);
\draw [-latex] (5,0) -- (6,0);
\draw [-latex] (6,0) -- (7,0);
\draw [-latex] (7,0) -- (8,0);
\draw [-latex] (8,0) -- (9,0);
\end{tikzpicture}}\]

The diene 1g was prepared according to the literature procedure.¹⁰ Analytical data matches the literature.¹⁰
Preparation of ethyl \((Z)-5-(1,3\text{-dioisoindolin-2-yl})-2-(1-(((\text{trifluoromethyl})sulfonyl)oxy)ethylidene)\)pentanoate (2q):

![Chemical structure of the target compound 2q]

To an oven dried 50 mL round bottom flask was added 168 mg of NaH (60% dispersion in mineral oil, 5.0 mmol, 1.0 equiv). The flask was purged with N\(_2\) and 15 mL of THF was added. Then 1.6 g of \(\beta\)-keto ester \(C\) (5.0 mmol, 1.0 equiv), dissolved in 5 mL of THF, was added dropwise. \(\text{Caution:} \) \(H_2\) is evolved during the addition. The reaction mixture was stirred for 15 min followed by addition of 2.0 g of PhNTf\(_2\) (5.6 mmol, 1.1 equiv) in one portion. The reaction mixture was stirred for 6 h followed by quenching with 5 mL of water. The reaction mixture was extracted with 1x50 mL of Et\(_2\)O, organic layer washed with 1x10 mL of brine, dried over MgSO\(_4\), and solvents evaporated under reduced pressure. The product was then purified by flash column chromatography (20→40% Et\(_2\)O:hexanes) to afford 2q as a colorless oil (1.40 g, 62% yield, \(Z\) isomer); \(R_f= 0.20\) (40% Et\(_2\)O:hexane). \(^1\)H NMR (500 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 7.80 (d, \(J = 5.0\) Hz, 2H), 7.71 (d, \(J = 5.0\) Hz, 2H), 4.20 (q, \(J = 6.7\) Hz, 2H), 3.69 (t, \(J = 7.5\) Hz, 2H), 2.39 (t, \(J = 7.5\) Hz, 2H), 2.13 (s, 3H), 1.84 (quint, \(J = 7.5\) Hz, 2H), 1.25 (t, \(J = 5.0\) Hz, 3H); \(^{13}\)C NMR (126 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 168.5, 165.3, 148.6, 134.4, 132.5, 126.3, 123.4, 118.8 (q, \(J_C^F = 320.9\) Hz), 62.1, 37.7, 27.6, 27.4, 17.7, 14.1; ATR-FTIR (neat): 3392, 2933, 2360, 2342, 1772, 1707, 1616, 1513, 1396, 1265, 1214, 1170, 1078, 1036, 886, 733, 720, 702, 668. HRMS (ESI) m/z (M+Na\(^+\)) calculated for C\(_{18}\)H\(_{18}\)NO\(_7\)NaSF\(_3\): 472.0654 observed: 472.0662.

Preparation of ethyl \((Z)-2\text{-methyl-3-(((\text{trifluoromethyl})sulfonyl)oxy)-5-(trimethylsilyl)pent-2-enoate}\) (2r):

![Chemical structure of the target compound 2r]

To a 1.3 g of NaH (60% dispersion in mineral oil, 39 mmol, 1.3 equiv) was added 60 mL of THF. To this mixture, 4.2 mL of \(\beta\)-keto ester \(D\) (30 mmol, 1.0 equiv) was added dropwise and the resulting suspension was stirred for 15 min. \(^{11}\) The reaction mixture was then cooled to 0 °C and 14.4 mL of a \(n\)-BuLi solution (2.5 M solution in hexanes, 36.0 mmol, 1.2 equiv) was added. After stirring for 30 min at 0 °C, 4.9 mL of (iodomethy)trimethylsilane (33 mmol, 1.1 equiv) was added in one portion. The mixture
was allowed to warm to room temperature and stirred for 2 h followed by quenching with 10 mL of 5% H$_2$SO$_4$. The organic layer was separated and the aqueous layer was extracted with Et$_2$O (2X50 mL). The combined organic layers were washed with brine (1X30 mL), dried over MgSO$_4$, and concentrated under vacuum. The product was then purified by flash column chromatography (3→6% EtOAc:hexanes) to afford E as a colorless oil (5.0 g, 72% yield); R$_f$ = 0.28 (6% EtOAc:hexanes). $^1$H NMR (500 MHz, CDCl$_3$) δ 4.18 (q, J = 8.3 Hz, 2H), 3.54 (q, J = 8.3 Hz, 1H), 2.59-2.36 (m, 2H), 1.33 (d, J = 5.0 Hz, 13C NMR (126 MHz, CDCl$_3$) δ 206.7, 170.7, 61.3, 52.3, 36.3, 14.2, 13.1, 10.1, -1.8; ATR-FTIR (neat); 2953, 2897, 2360, 2342, 1743, 1715, 1456, 1410, 1376, 1248, 1178, 1070, 832, 755, 691, 668. HRMS (ESI) m/z (M+Na)$^+$ calculated for C$_{11}$H$_{22}$O$_3$NaSi: 253.1236 observed: 253.1233.

The synthesis of 2r was achieved following the same procedure as that of 2q, using 1.1 g of β-keto ester E (5.0 mmol, 1.0 equiv), 185 mg of NaH (60% dispersion in mineral oil, 5.5 mmol, 1.1 equiv), 2.0 g of PhNTf$_2$ (5.5 mmol, 1.1 equiv) and 10 mL of THF. The product was then purified by flash column chromatography (2→4% EtOAc:hexanes) to afford 2r as a colorless oil (1.2 g, 67% yield, Z isomer); R$_f$ = 0.33 (6% EtOAc:hexanes). $^1$H NMR (300 MHz, CDCl$_3$) δ 4.27 (q, J = 7.0 Hz, 2H), 2.37 (t, J = 9.0 Hz, 2H), 1.97 (s, 3H), 1.32 (t, J = 6.0 Hz, 3H), 0.79 (t, J = 9.0 Hz, 2H), 0.03 (s, 9H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 165.7, 153.6, 120.5, 118.5 (q, $^1$J$_{CF}$ = 320.5 Hz), 61.8, 26.0, 15.0, 14.0, 13.6, -2.1; ATR-FTIR (neat); 2956, 2360, 2343, 1723, 1660, 1420, 1247, 1204, 1137, 1098, 1029, 909, 830, 759, 601. HRMS (ESI) m/z (M+Na)$^+$ calculated for C$_{12}$H$_{21}$O$_5$NaSSiF$_3$: 385.0729 observed: 385.0733.

**Preparation of ethyl (E)-3-(((trifluoromethyl)sulfonyl)oxy)-2-((trimethylsilyl)methyl)but-2-enoate (2t):**

\[
\text{NaH, PhNTf}_2 \quad \text{THF, rt} \quad \text{OTf} \quad \text{SiMe}_3
\]

The same procedure as used for the synthesis of 2q was followed using 1.1 g of β-keto ester F (5.0 mmol, 1.0 equiv), 185 mg of NaH (60% dispersion in mineral oil, 5.5 mmol, 1.1 equiv), 2.0 g of PhNTf$_2$ (5.5 mmol, 1.1 equiv) and 10 mL of THF. The product was then purified by flash column chromatography (1→2% EtOAc:hexanes) to afford 2t as a colorless oil (1.2 g, 70% yield, Z isomer); R$_f$ = 0.38 (6% EtOAc:hexanes). $^1$H NMR (500 MHz, CDCl$_3$) δ 4.22 (q, J = 8.3 Hz, 2H), 2.02 (s, 3H), 1.76 (s, 2H), 1.29 (t, J = 7.5 Hz, 3H), 0.03 (s, 9H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 166.0, 143.9, 125.7, 122.4, 119.8, 117.3, 114.8, 61.8, 20.2, 17.7, 14.0, -1.3; ATR-FTIR (neat); 2959, 2360, 2342, 1724, 1419, 1293, 1248, 1203, 1137,
HRMS (ESI) m/z (M+Na)$^+$ calculated for C$_{11}$H$_{19}$O$_3$NaSiF$_3$: 371.0572 observed: 371.0576.

**Preparation of (E)-4-hydroxy-3-methylbut-2-en-2-yl trifluoromethanesulfonate (2w):**

\[
\begin{align*}
\text{OTf} & \quad \text{DIBAL, Et$_2$O} \\
\text{O} & \quad \text{-78 °C → rt} \\
\text{2v} & \quad \text{OH} \\
\text{OTf} & \quad \text{2w}
\end{align*}
\]

The representative procedure developed by Meyer and co-workers$^{12}$ was followed to synthesize 2w using 414 mg (1.5 mmol, 1.0 equiv) of 2v, 2.2 mL of DIBAL-H (25 wt.% in toluene, ≈2.2 equiv) and 10 mL of Et$_2$O (instead of THF). The product was then purified by flash column chromatography (20→30% Et$_2$O:hexanes) to afford 2w as a light yellow oil (286 mg, 81% yield); $R_f$ = 0.16 (30% Et$_2$O:hexanes); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.15 (s, 2H), 2.10 (s, 3H), 2.01 (br, 1H), 1.87 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.7, 128.1, 118.5 (q, $^1$J$_{CF}$ = 317.7 Hz), 62.7, 16.6, 14.6; ATR-FTIR (neat): 3355, 1696, 1408, 1200, 1130, 1084, 1012, 905, 817, 767, 631. HRMS (ESI) m/z (M+Na)$^+$ calculated for C$_6$H$_9$O$_4$NaSF$_3$: 257.0074 observed: 257.0074.

**Preparation of (Z)-4-hydroxy-3-methylbut-2-en-2-yl trifluoromethanesulfonate (2x):**

\[
\begin{align*}
\text{OTf} & \quad \text{DIBAL, Et$_2$O} \\
\text{O} & \quad \text{-78 °C → rt} \\
\text{2p} & \quad \text{OH} \\
\text{OTf} & \quad \text{2x}
\end{align*}
\]

The general procedure used to synthesize 2w was employed using 829 mg (3.0 mmol, 1.0 equiv) of 2p, 4.4 mL of DIBAL-H (25 wt.% in toluene, ≈2.2 equiv) and 20 mL of Et$_2$O. The product was then purified by flash column chromatography (20→30% Et$_2$O:hexanes) to afford 2x as a light yellow oil (573 mg, 81% yield); $R_f$ = 0.26 (30% Et$_2$O:hexanes); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.19 (s, 2H), 2.05 (s, 4H, $-CH_3$ and $-OH$ overlapping), 1.83 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 141.1, 128.4, 118.5 (q, $^1$J$_{CF}$ = 317.7 Hz), 60.8, 16.7, 15.2; ATR-FTIR (neat): 3355, 1696, 1410, 1203, 1135, 1084, 1012, 905, 817, 767, 631. HRMS (ESI) m/z (M+Na)$^+$ calculated for C$_6$H$_9$O$_4$NaSF$_3$: 257.0071 observed: 257.0074.

**Preparation of (E)-1-(dimethoxyphosphoryl)prop-1-en-2-yl trifluoromethanesulfonate:**

S7
The representative procedure developed by Frantz and co-workers$^4$ for the synthesis of $E$-enol triflates was employed, using 1.28 g of $\beta$-keto phosphonate $G$ (7.68 mmol, 1.0 equiv), 3.23 mL of Tf$_2$O (19.2 mmol, 2.5 equiv), 13.8 mL of Me$_4$NOH (25% solution in H$_2$O, 38.4 mmol, 5.0 equiv) and 40 mL of toluene. The product was then purified by flash column chromatography (60→80% EtOAc:hexane) to afford $2z$ as a colorless oil (458 mg, 20% yield, $E$ isomer); $R_f = 0.45$ (70% EtOAc:hexanes). The low yield is likely due to product decomposition on the silica gel column.$^{13}$ $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.61 (dd, $J = 4.25$, 0.75 Hz, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 2.45 (d, $J = 2.5$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.9 (d, $J = 27.7$ Hz), 118.6 (d, $J = 320.0$ Hz), 107.5 (d, $J = 190.3$ Hz), 52.9 (d, $J = 6.3$ Hz), 19.4 (d, $J = 1.3$ Hz); ATR-FTIR (neat); 2959, 1660, 1419, 1244, 1100, 1023, 991, 933, 780, 742, 608. HRMS (ESI) m/z (M+Na)$^+$ calculated for C$_{6}$H$_{10}$O$_{6}$NaPSF$_3$: 320.9786 observed: 320.9795.

Preparation of ethyl ($E$)-3-(((trifluoromethyl)sulfonyl)oxy)-5-(trimethylsilyl)pent-2-enoate ($2ab$):

```
Me$_3$Si
\begin{align*}
| & \text{NaH, PhNTf$_2$} \\
| & \text{DMF, rt} \\
\end{align*}
\text{H}
\rightarrow
\text{Me$_3$Si}
\text{O}
\begin{align*}
| & \text{NaH, PhNTf$_2$} \\
| & \text{DMF, rt} \\
\end{align*}
\text{2ab}
```

To an oven dried 20 mL scintillation vial was added 148 mg of NaH (60% dispersion in mineral oil, 4.4 mmol, 1.1 equiv).$^{14}$ The vial was purged with nitrogen and 5 mL of DMF was added. Then 865 mg of $\beta$-keto ester $H$ (4.0 mmol, 1.0 equiv) dissolved in 1 mL of DMF was added drop wise. Caution: H$_2$ is evolved during the addition. The reaction mixture was stirred for 15 min followed by addition of 1.6 g of PhNTf$_2$ (4.4 mmol, 1.1 equiv) in one portion. The reaction mixture was stirred for 6 h followed by quenching with 5 mL of water. The reaction mixture was extracted with 1x50 mL of Et$_2$O, organic layer washed with 1x10 mL of brine, dried over MgSO$_4$, and solvents evaporated under reduced pressure. The product was then purified by flash column chromatography (1→2% Et$_2$O:hexanes) to afford $2ab$ as a colorless oil (976 mg, 70% yield, $E$ isomer); $R_f = 0.51$ (2% EtOAc:hexanes). $^1$H NMR (500 MHz, CD$_2$Cl$_2$) $\delta$ 5.83 (s, 1H), 4.18 (q, $J = 6.7$ Hz, 2H), 2.86 (t, $J = 7.5$ Hz, 2H), 1.27 (t, $J = 7.5$ Hz, 3H), 0.80 (t, $J = 7.5$ Hz, 2H), 0.02 (s, 9H); $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$) $\delta$ 168.1, 164.2, 118.6 (q, $J_CF = 320.5$ Hz), 111.3, 61.2, 26.3, 14.2, 13.7, -2.03; ATR-FTIR (neat); 2957, 2360, 1726, 1662, 1422, 1247, 1204, 1138, 1028, 972, 926, 859, 834, 712, 640. HRMS (ESI) m/z (M+Na)$^+$ calculated for C$_{11}$H$_{19}$O$_5$NaSiSF$_3$: 371.0572 observed: 371.0574.
General procedure for the optimization of 1,2-hydrovinylation of 1,3-diene with cyclic enol nonaflate:

The general procedure A described below was used with the following modifications. The reaction was performed on 0.20 mmol scale with ≈ 10 wt% internal standard (2-methoxynaphthalene). After work-up the reaction mixture was analysed for product formation by $^1$H NMR. The modifications described below were applied in order to optimize the reaction.

![Chemical diagram](image)

| entry | solvent | "hydride source" | % conv. 2a | % yield (3a/4a) |
|-------|---------|------------------|------------|-----------------|
| 1     | DMA     | HCO$_2$NH$_4$    | 53         | 5 (nd)          |
| 2     | DMA     | (HCO$_2$)$_2$Zn  | 69         | 52 (15:4:1)     |
| 3     | DMA     | HCO$_2$LiH$_2$O  | 57         | 46 (16:1)       |
| 4     | DMA     | HCO$_2$Na        | >95        | 62 (16:1)       |
| 5     | DMA     | Et$_3$SiH        | 93         | 59 (9:6:1)      |
| 6     | DMA     | (EtO)$_2$SiH     | 84         | 27 (8:8:1)      |
| 7     | THF     | HCO$_2$Na        | 28         | 4 (nd)          |
| 8     | t-AmOH  | HCO$_2$Na        | 48         | 10 (20:1)       |
| 9     | DMA     | HCO$_2$Na        | >95        | 79 (15:1)       |
| 10    | DMA     | HCO$_2$Na        | >95        | 78 (15:1)       |
| 11    | DMA     | HCO$_2$K         | >95        | 68 (11:1)       |

a) Determined by NMR using an internal standard on 0.2 mmol scale. b) Yields are a combination of both 3a and 4a. c) Reaction performed with 0.75 equiv of zinc formate. d) Reaction performed in a concentration of 0.33 M in 2a. e) Reaction performed using 2 mol% Pd$_2$dba$_3$·CHCl$_3$. Reaction performed on 0.5 mmol scale gave 75% yield (both 3a and 4a) and 15:1 regioselectivity.

General procedure A for the 1,2-hydrovinylation of 1,3-dienes with cyclic enol nonaflates (or triflates):

To a 4 mL oven dried vial with a stir bar was added diene (0.5 mmol, 1.0 equiv), vinyl nonaflate/triflate (0.5 mmol, 1.0 equiv), 51.0 mg of sodium formate (0.75 mmol, 1.5 equiv), and 10.4 mg of Pd$_2$dba$_3$·CHCl$_3$ (0.01 mmol, 0.02 equiv). The vial was sealed with a phenolic screw cap fitted with a septa. The vial was then evacuated and filled with nitrogen. This cycle was repeated three times followed by addition of 1.5 mL of DMA via syringe. Further, parafilm was wrapped around the cap to make the vial air tight. The vial suspension was then allowed to stir at room temperature for 16 h followed by filtration through a plug of silica gel with 20 mL of methy tert-butyl ether (MTBE). The solution was transferred to a separatory funnel and further diluted with 30 mL of MTBE and washed with 3x10 mL of water and finally with brine.
(1x10 mL). The organic layer was dried over anhydrous MgSO₄ followed by removal of solvents under reduced pressure. The ¹H NMR of the crude reaction mixture was taken at this stage to determine the reported regio-selectivity of the reduction. The product was then purified by flash column chromatography. *Note:* Yields are reported as a mixture of isomers.

![3a](image)

**3a**

**{(E)-4-(4-phenylbut-3-en-1-yl)-3,6-dihydro-2H-pyran (3a)}**: The general procedure A was followed using 65.0 mg of diene (0.5 mmol, 1.0 equiv) and 191.0 mg of enol nonaflate (0.5 mmol, 1.0 equiv). The product was then purified by flash column chromatography (0→2% EtOAc:hexanes) to afford 3a as a colorless oil (80 mg, 75% yield, 3a:4a::15:1), Rₙ = 0.13 (2% EtOAc:hexanes). ¹H NMR (300 MHz, CDCl₃) δ 7.37-7.18 (m, 5H), 6.42 (d, J = 18.0 Hz, 1H), 6.23 (td, J = 18.0, 6.0 Hz, 1H), 5.48 (m, 1H), 4.16-4.12 (m, 2H), 3.81 (t, J = 6.0 Hz, 2H), 2.37 (q, J = 7.0 Hz, 2H), 2.18 (t, J = 7.5 Hz, 2H), 2.12-2.08 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 137.9, 135.2, 130.3, 128.6, 127.1, 126.1, 120.2, 65.6, 64.5, 37.0, 31.0, 28.8; ATR-FTIR (neat); 3023, 2921, 2845, 2360, 2342, 1494, 1383, 1126, 962, 849, 741, 691. HRMS (ESI) m/z (M+H)⁺ calculated for C₁₅H₁₉O: 215.1436 observed: 215.1434.

![4a](image)

**4a**

**{(E)-4-(4-phenylbut-2-en-1-yl)-3,6-dihydro-2H-pyran (4a)}**: ¹H NMR (300 MHz, CDCl₃) δ 7.31-7.17 (m, 5H), 5.68-5.58 (m, 1H), 5.53-5.43 (m, 2H), 4.12-4.11 (m, 2H), 3.77 (t, J = 4.5 Hz, 2H), 3.36 (d, J = 6.0 Hz, 2H), 2.71 (d, J = 6.0 Hz, 2H), 2.08-2.00 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 140.9, 134.9, 131.4, 128.7 (128.73), 128.7 (128.69), 128.6, 126.2, 120.5, 65.8, 64.6, 40.4, 39.2, 28.7; ATR-FTIR (neat); 3023, 2921, 2845, 2360, 2342, 1494, 1383, 1126, 962, 849, 741, 691. HRMS (ESI) m/z (M+H)⁺ calculated for C₁₅H₁₉O: 215.1436 observed: 215.1434.
**Tert-butyl (E)-4-(4-phenylbut-3-en-1-yl)-3,6-dihydropyridine-1(2H)-carboxylate (3b):** The general procedure A was followed using 65 mg of diene (0.5 mmol, 1.0 equiv) and 241 mg of enol nonaflate (0.5 mmol, 1.0 equiv). The product was then purified by flash column chromatography (2→4% EtOAc:hexanes) to afford 3b as a colorless oil (128 mg, 82% yield, 10:1), R<sub>f</sub> = 0.42 (10% EtOAc:hexanes).

1H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.33-7.25 (m, 4H), 7.18 (t, J = 8.0 Hz, 1H), 6.38 (d, J = 16.0 Hz, 1H), 6.19 (td, J = 16.0, 6.0 Hz, 1H), 5.42-5.35 (m, 1H), 3.89-3.82 (m, 2H), 3.49 (t, J = 6.0 Hz, 2H), 2.32 (q, J = 6.7 Hz, 2H), 2.16 (t, J = 8.0 Hz, 2H), 2.07-2.03 (m, 2H), 1.46 (s, 9H); 13C NMR (100 MHz, CDCl<sub>3</sub>, 50 °C) δ 155.2, 138.1, 136.3, 130.5, 128.7, 127.1, 126.1, 118.6, 79.6, 43.6, 40.6, 37.2, 31.2, 29.9, 28.7; ATR-FTIR (neat); 3380, 2970, 2928, 2360, 2342, 1684, 1419, 1366, 1240, 1163, 1112, 951, 692, 669. HRMS (ESI) m/z calculated for C<sub>20</sub>H<sub>27</sub>NO<sub>2</sub>Na: 336.1939 observed 336.1943.

(3c)

**3c** (E)-4-(4-phenylbut-3-en-1-yl)-1-tosyl-1,2,3,6-tetrahydropyridine (3c): The general procedure A was followed using 65 mg of diene (0.5 mmol, 1.0 equiv) and 268 mg of enol nonaflate (0.5 mmol, 1.0 equiv). The product was then purified by flash column chromatography (5→8% EtOAc:hexanes) to afford 3c as a white solid (118 mg, 64% yield, 9.1:1), Mp = 137 °C, R<sub>f</sub> = 0.23 (10% EtOAc:hexanes). 1H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.66 (d, J = 8.0 Hz, 2H), 7.31-7.25 (m, 7H), 7.19 (t, J = 6.0 Hz, 1H), 6.35 (d, J = 16.0 Hz, 1H), 6.13 (td, J = 16.0, 8.0 Hz, 1H), 5.36-5.34 (m, 1H), 3.56-3.54 (m, 2H), 3.18 (t, J = 6.0 Hz, 2H), 2.41 (s, 3H), 2.26 (q, J = 8.0 Hz, 2H), 2.16-2.09 (m, 4H); 13C NMR (100 MHz, CDCl<sub>3</sub>) δ 143.6, 138.0, 136.3, 134.3, 130.7, 130.0, 129.8, 128.7, 128.0, 127.2, 126.2, 117.2, 45.0, 43.1, 36.9, 31.1, 28.8, 21.7; ATR-FTIR (neat); 3380, 2970, 2820, 2360, 2342, 1653, 1597, 1473, 1340, 1165, 962, 682, 669. HRMS (ESI) m/z (M+Na)<sup>+</sup> calculated for C<sub>22</sub>H<sub>25</sub>NO<sub>2</sub>SNa: 390.1504 observed: 390.1508

(3d)

**Benzyl (E)-4-(4-phenylbut-3-en-1-yl)-3,6-dihydropyridine-1(2H)-carboxylate (3d):** The general procedure A was followed using 65 mg of diene (0.5 mmol, 1.0 equiv) and 258 mg of enol nonaflate (0.5 mmol, 1.0 equiv). The product was then purified by flash column chromatography (5→10%...
EtOAc:hexanes) to afford 3d as a colorless oil (136 mg, 78% yield, 13.6:1), Rf = 0.17 (10% EtOAc:hexanes).

1H NMR (500 MHz, CDCl₃) δ 7.39-7.29 (m, 9H), 7.21 (t, J = 7.5 Hz, 1H), 6.41 (d, J = 15.0 Hz, 1H), 6.21 (td, J = 15.0, 7.5 Hz, 1H), 5.46-5.39 (m, 1H), 5.17 (s, 2H), 3.98-3.96 (m, 2H), 3.62-3.59 (m, 2H), 2.35 (q, J = 8.3 Hz, 2H), 2.20-2.10 (m, 4H); 13C NMR (100 MHz, CDCl₃, 50 ºC) δ 155.7, 138.0, 137.3, 136.4, 130.6, 130.2, 128.7 (128.69), 128.7 (128.66), 128.1 (128.11), 128.1 (128.06), 127.1, 126.2, 118.2, 67.2, 43.6, 40.9, 37.2, 31.2, 28.6; ATR-FTIR (neat): 3025, 2899, 2838, 2360, 2342, 1698, 1420, 1281, 1233, 1105, 963, 742, 694, 668. HRMS (ESI) m/z (M+H)⁺ calculated for C₂₃H₂₆NO₂: 348.1964 observed: 348.1969.

3e

**((E)-4-(4-(4-methoxyphenyl)but-3-en-1-yl)-1,2,3,6-tetrahydro-1,1'-biphenyl (3e):** The general procedure A was followed using 80 mg of diene (0.5 mmol, 1.0 equiv) and 228 mg of enol nonaflate (0.5 mmol, 1.0 equiv). The product was then purified by flash column chromatography (10→20% Benzene:hexanes) to afford 3e as a colorless oil (110 mg, 69% yield, 10.8:1), Rf = 0.55 (10% EtOAc:hexanes). 1H NMR (500 MHz, CDCl₃) δ 7.33-7.19 (m, 7H), 6.86 (d, J = 10.0 Hz, 2H), 6.38 (d, J = 15.0 Hz, 1H), 6.12 (td, J = 15.0, 5.0 Hz, 1H), 5.56-5.54 (m, 1H), 3.82 (s, 3H), 2.81-2.72 (m, 1H), 2.37-2.30 (m, 3H), 2.20-2.07 (m, 5H), 2.00-1.97 (m, 1H), 1.83-1.75 (m, 1H); 13C NMR (126 MHz, CDCl₃) δ 158.9, 147.5, 137.4, 130.9, 129.4, 128.8, 128.5, 127.2, 127.1, 126.1, 121.1, 114.2, 55.5, 40.4, 37.8, 33.7, 31.6, 30.3, 29.2; ATR-FTIR (neat): 2914, 2834, 2400, 2342, 1605, 1510, 1249, 1176, 1029, 969, 847, 700, 669. HRMS (ESI) m/z (M+Na)⁺ calculated for C₂₃H₂₇ONa: 341.1881 observed: 341.1883.

3f

**((E)-9-(4-(4-methoxyphenyl)but-3-en-1-yl)-3,3-dimethyl-1,5-dioxaspiro[5.5]undec-8-ene (3f):** The general procedure A was followed using 80 mg of diene (0.5 mmol, 1.0 equiv) and 240.0 mg of enol nonaflate (0.5 mmol, 1.0 equiv). The product was then purified by flash column chromatography (2→4% EtOAc:hexanes) to afford 3f as a white solid (113 mg, 66% yield, 12:1), Mp = 113 ºC, Rf = 0.33 (10%
EtOAc:hexanes). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.26 (d, $J$ = 10.0 Hz, 2H), 6.83 (d, $J$ = 10.0 Hz, 2H), 6.32 (d, $J$ = 15.0 Hz, 1H), 6.10-6.04 (m, 1H), 5.32-5.28 (m, 1H), 3.79 (s, 3H), 3.59 (d, $J$ = 15.0 Hz, 2H), 3.49 (d, $J$ = 15.0 Hz, 2H), 2.38-2.34 (m, 2H), 2.30 (q, $J$ = 6.7 Hz, 2H), 2.13-2.08 (m, 4H), 1.97 (t, $J$ = 7.5 Hz, 2H), 1.03 (s, 3H), 0.92 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 158.8, 137.1, 130.8, 129.4, 128.6, 127.2, 117.5, 114.0, 97.5, 70.5, 55.5, 37.0, 35.0, 30.5, 27.7, 26.9, 23.1, 22.6; ATR-FTIR (neat); 2953, 2360, 2342, 1772, 1647, 1248, 1113, 669. HRMS (ESI) m/z (M+Na)$^+$ calculated for C$_{22}$H$_{30}$O$_3$Na: 365.2093 observed: 365.2096.

(\textit{E})-4-(4-(cyclopent-1-en-1-yl)but-1-en-1-yl)phenol (3g): The general procedure A was followed using 73 mg of diene (0.5 mmol, 1.0 equiv) and 183 mg of enol nonaflate (0.5 mmol, 1.0 equiv). The product was then purified by flash column chromatography (5→10% EtOAc:hexanes) to afford 3g as a white solid (79 mg, 74% yield, 12.6:1), Mp = 62-64 °C, $R_f$ = 0.19 (10% EtOAc:hexanes). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.22 (d, $J$ = 10.0 Hz, 2H), 6.76 (d, $J$ = 10.0 Hz, 2H), 6.33 (d, $J$ = 20.0 Hz, 1H), 6.09 (td, $J$ = 15.0, 7.5 Hz, 1H), 5.39-5.37 (m, 1H), 4.70 (s, 1H), 2.36-2.21 (m, 8H), 1.86 (quint, $J$ = 7.5 Hz, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 154.7, 144.4, 131.2, 129.3, 128.9, 127.4, 123.8, 115.5, 35.4, 32.7, 31.6, 31.4, 23.7; ATR-FTIR (neat); 3423, 2926, 2846, 2360, 2342, 1609, 1511, 1437, 1263, 1171, 963, 734, 703, 668. HRMS (ESI) m/z (M+H)$^+$ calculated for C$_{15}$H$_{19}$O: 215.1436 observed: 215.1430.

(\textit{E})-4-(4-(cyclohept-1-en-1-yl)but-1-en-1-yl)phenol (3h): The general procedure A was followed using 73 mg of diene (0.5 mmol, 1.0 equiv) and 197 mg of enol nonaflate (0.5 mmol, 1.0 equiv). The product was then purified by flash column chromatography (10→12% EtOAc:hexanes) to afford 3h as a white solid (81 mg, 67% yield, 9.7:1), Mp = 68-70 °C, $R_f$ = 0.23 (10% EtOAc:hexanes). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.23 (d, $J$ = 5.0 Hz, 2H), 6.77 (d, $J$ = 5.0 Hz, 2H), 6.33 (d, $J$ = 15.0 Hz, 1H), 6.08 (td, $J$ = 15.0, 7.5 Hz, 1H), 5.59 (t, $J$ = 7.5 Hz, 1H), 4.80 (br, 1H), 2.28 (q, $J$ = 8.3 Hz, 2H), 2.15-2.07 (m, 6H), 1.74 (quint, $J$ = 6.3 Hz, 2H), 1.53-1.45 (m, 4H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 154.6, 144.3, 131.3, 129.2, 129.0, 127.4, 126.5, 115.6, 40.4, 33.1, 32.9, 32.0, 28.5, 27.6, 27.0; ATR-FTIR (neat); 3317, 2916, 2844, 2360, 2342, 1608,
4-{(E)-4-[(1R,4S)-1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl]but-1-en-1-yl]phenol (3i): The general procedure A was followed using 73 mg of diene (0.5 mmol, 1.0 equiv) and 142 mg of enol triflate (0.5 mmol, 1.0 equiv). The product was then purified by flash column chromatography (5→10% EtOAc:hexanes) to afford 3i as a colorless oil (114 mg, 81% yield, >20:1), Rf = 0.13 (5% EtOAc:hexanes). 

$^1$H NMR (500 MHz, CD$_2$Cl$_2$) δ 7.22 (d, $J = 10.0$ Hz, 2H), 6.76 (d, $J = 6.5$ Hz, 2H), 6.34 (d, $J = 15.0$ Hz, 1H), 6.13 (td, $J = 15.0$, 5.0 Hz, 1H), 5.60 (m, 1H), 5.07 (br, 1H), 2.38-2.27 (m, 2H), 2.23 (t, $J = 2.5$ Hz, 1H), 2.17-2.05 (m, 2H), 1.83 (dt, $J = 7.5$, 3.5 Hz, 1H), 1.49 (t, $J = 8.5$ Hz, 1H), 0.98 (s, 3H), 0.95 (d, $J = 8.0$ Hz, 2H), 0.80 (s, 3H), 0.77 (s, 3H); $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$) δ 155.0, 149.4, 131.3, 129.3 (129.29), 129.3 (129.27), 127.5, 126.9, 115.7, 56.6, 54.6, 51.8, 31.7, 31.0, 28.0, 26.4, 19.9 (19.91), 19.9 (19.85), 11.6; ATR-FTIR (neat); 2952, 2360, 2342, 1700, 1653, 1559, 1540, 1457, 1264, 1171, 966, 733, 703, 669. HRMS (ESI) m/z (M+H)$^+$ calculated for C$_{20}$H$_{27}$O: 283.2062 observed: 283.2075.

5-{(E)-4-[(8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1H-cyclopenta[a]phenanthren-3-yl]but-1-en-1-yl}-2-methoxyphenol (3j): The general procedure A was followed using 53 mg of diene (0.3 mmol, 1.0 equiv), 155 mg of enol triflate (0.3 mmol, 1.0 equiv), 31 mg of sodium formate (0.45 mmol, 1.5 equiv), 6.2 mg of Pd$_2$dba$_3$·CHCl$_3$ (0.006 mmol, 0.02 equiv) and 0.9 mL of DMA. The product was then purified by flash column chromatography (5→10% EtOAc:hexanes) to afford 3j as a light yellow solid (137 mg, 84% yield, 17.6:1), Mp = 126-129 °C, Rf = 0.24 (10% EtOAc:hexanes). $^1$H NMR (500 MHz, CDCl$_3$) δ 6.96 (d, $J = 5.0$ Hz,
1H), 6.80-6.76 (m, 2H), 6.29 (d, J = 20.0 Hz, 1H), 6.07 (td, J = 15.0, 7.5 Hz, 1H), 5.75 (s, 1H), 5.54 (s, 1H), 5.33-5.32 (m, 1H), 3.87 (s, 3H), 2.33 (q, J = 8.3 Hz, 2H), 2.21-2.14 (m, 4H), 2.05-1.97 (m, 3H), 1.86-1.80 (m, 2H), 1.67-1.50 (m, 5H), 1.44-0.97 (m, 15H), 0.93-0.92 (m, 6H), 0.87 (d, J = 5.0 Hz, 6H), 0.70 (s, 3H); 13C NMR (126 MHz, CDCl$_3$) δ 145.9, 145.8, 142.1, 136.4, 132.0, 129.5, 129.2, 124.6, 121.7, 118.5, 111.8, 110.8, 57.2, 56.4, 56.1, 48.6, 42.7, 40.1, 39.8, 37.5, 36.4, 36.0, 35.1, 34.4, 32.1, 32.0, 31.7, 28.5, 28.3, 26.6, 24.4, 24.1, 23.1, 22.8, 21.4, 19.1, 19.0, 12.2; ATR-FTIR (neat); 2934, 2360, 2342, 1790, 1507, 1456, 1419, 1359, 1220, 1092, 1028, 901, 668. HRMS (ESI) m/z (M+Na)$^+$ calculated for C$_{38}$H$_{56}$O$_2$Na: 567.4178 observed: 567.4189.

5-((E)-4-((4R,4aS,6R)-4,4a-dimethyl-6-(prop-1-en-2-yl)-3,4,4a,5,6,7-hexahydronaphthalen-2-yl)but-1-en-1-yl)-2-methoxyphenol (3k): The general procedure A was followed using 53 mg of diene (0.3 mmol, 1.0 equiv), 105 mg of enol triflate (0.3 mmol, 1.0 equiv), 31 mg of sodium formate (0.45 mmol, 1.5 equiv), 6.2 mg of Pd$_2$dba$_3$·CHCl$_3$ (0.006 mmol, 0.02 equiv) and 0.9 mL of DMA. The product was then purified by flash column chromatography (3→6% EtOAc:hexanes) to afford 3k as a colorless oil (98 mg, 86% yield, 11.5:1), R$_f$ = 0.29 (10% EtOAc:hexanes). $^1$H NMR (500 MHz, CDCl$_3$) δ 6.96 (s, 1H), 6.80-6.76 (m, 2H), 6.30 (d, J = 15.0 Hz, 1H), 6.06 (td, J = 15.0, 7.5 Hz, 1H), 5.78 (s, 1H), 5.38-5.36 (m, 1H), 4.75 (d, J = 5.0 Hz, 2H), 3.87 (s, 3H), 2.46-2.40 (m, 1H), 2.33 (q, J = 6.6 Hz, 2H), 2.26-2.15 (m, 3H), 2.00-1.93 (m, 4H), 1.54 (sex, J = 8.3 Hz, 1H), 1.18 (t, J = 12.5 Hz, 1H), 0.91 (d, J = 5.0 Hz, 3H), 0.88 (s, 3H); 13C NMR (126 MHz, CDCl$_3$) δ 150.7, 145.9, 145.8, 142.6, 137.2, 131.9, 129.6, 129.1, 124.3, 121.3, 118.5, 111.8, 110.8, 108.7, 56.2, 40.4, 39.3, 37.6, 37.3, 36.1, 35.8, 31.5, 31.4, 20.9, 17.6, 15.0; ATR-FTIR (neat); 3320, 2971, 2874, 2359, 1643, 1584, 1510, 1441, 1381, 1268, 1118, 1030, 962, 884, 792, 760, 733, 640. HRMS (ESI) m/z (M+Na)$^+$ calculated for C$_{28}$H$_{46}$O$_2$Na: 401.2457 observed: 401.2470.
2-methoxy-5-((E)-4-((8S,9S,13S,14S)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15-octahydro-6H-cyclopenta[a]phenanthren-17-yl)but-1-en-1-yl)phenol (3l): The general procedure A was followed using 53 mg of diene (0.3 mmol, 1.0 equiv) and 125 mg of enol triflate (0.3 mmol, 1.0 equiv), 31 mg of sodium formate (0.45 mmol, 1.5 equiv), 6.2 mg of Pd$_2$dba$_3$·CHCl$_3$ (0.006 mmol, 0.02 equiv) and 0.9 mL of DMA. The product was then purified by flash column chromatography (6→10% EtOAc:hexanes) to afford 3l as a white solid (93 mg, 70% yield, >20:1), Mp = 110 °C, $R_f$ = 0.16 (10% EtOAc:hexanes). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.21 (d, $J$ = 10.0 Hz, 1H), 7.00 (d, $J$ = 5.0 Hz, 1H), 6.82-6.77 (m, 2H), 6.72 (dd, $J$ = 7.5, 2.5 Hz, 1H), 6.65 (s, 1H), 6.33 (d, $J$ = 20.0 Hz, 1H), 6.15 (td, $J$ = 15.0, 5.0 Hz, 1H), 5.57 (s, 1H), 5.40-5.37 (m, 1H), 3.88 (s, 3H), 3.79 (s, 3H), 2.96-2.84 (m, 2H), 2.43-2.15 (m, 6H), 1.96-1.86 (m, 3H), 1.64-1.40 (m, 6H), 0.80 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 157.6, 155.4, 146.0, 145.4, 138.3, 133.3, 132.0, 129.5, 129.4, 126.2, 121.7, 118.5, 114.0, 111.7, 111.6, 110.8, 56.6, 56.2, 55.4, 47.2, 44.7, 37.7, 34.9, 31.2, 30.0, 28.1, 27.2, 26.8, 16.1; ATR-FTIR (neat): 3545, 2927, 2838, 2360, 2342, 1635, 1507, 1457, 1266, 1210, 1030, 907, 729. HRMS (ESI) m/z (M+Na)$^+$ calculated for C$_{30}$H$_{36}$O$_3$Na: 467.2562 observed: 467.2570.

![Structure 3m](https://via.placeholder.com/150)

**3m**

Tert-butyl (E)-4-(4-cyclohexylbut-3-en-1-yl)-3,6-dihydropyridine-1(2H)-carboxylate (3m): The general procedure A was followed using 68 mg of diene (0.5 mmol, 1.0 equiv) and 241 mg of enol nonaflate (0.5 mmol, 1.0 equiv). The product was then purified by flash column chromatography (2% EtOAc:hexanes) to afford 3m as a colorless oil (97 mg, 61% yield, >20:1), $R_f$ = 0.39 (10% EtOAc:hexanes). $^1$H NMR (500 MHz, CDCl$_3$) δ 5.45-5.29 (m, 3H), 3.85 (m, 2H), 3.47 (m, 2H), 2.67 (d, $J$ = 5.0 Hz, 1H), 2.09-2.02 (m, 4H), 1.90 (t, $J$ = 7.5 Hz, 1H), 1.69-1.62 (m, 5H), 1.46 (s, 9H), 1.28-1.11 (m, 4H), 1.04 (q, $J$ = 11.7, 1H), 0.88 (q, $J$ = 11.7 Hz, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 155.2, 137.2, 131.4, 128.2, 127.1, 79.6, 43.6, 40.9, 40.7, 38.3, 37.5, 33.6, 33.4, 30.9, 28.8, 26.9, 26.6, 26.5, 26.3; ATR-FTIR (neat): 2974, 2920, 2849, 2360, 2342, 1696, 1417, 1364, 1237, 1169, 1109, 968, 866, 768, 668. HRMS (ESI) m/z (M+Na)$^+$ calculated for C$_{20}$H$_{33}$O$_2$NNa: 342.2409 observed: 342.2406.
Tert-butyl 4-(2-(4,4-dimethylcyclohex-1-en-1-yl)ethyl)-3,6-dihydropyridine-1(2H)-carboxylate (3n): The general procedure A was followed using 68 mg of diene (0.5 mmol, 1.0 equiv) and 241 mg of enol nonaflate (0.5 mmol, 1.0 equiv). The product was then purified by flash column chromatography (2% EtOAc:hexanes) to afford 3n as a colorless oil (92 mg, 58% yield, 5.4:1), $R_f = 0.39$ (10% EtOAc:hexanes); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.32-5.28 (m, 2H), 3.82 (m, 2H), 3.45 (t, $J = 5.0$ Hz, 2H), 2.12-2.03 (m, 6H), 1.92 (t, $J = 7.5$ Hz, 2H), 1.74 (d, $J = 1.5$ Hz, 2H), 1.45 (s, 9H), 1.33 (t, $J = 5.0$ Hz, 2H), 0.86 (s, 6H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 155.2, 135.9, 120.5, 117.9, 79.5, 41.2, 40.4, 35.9, 35.8, 35.7, 35.1, 33.1, 28.7, 28.4, 26.3, 24.7; ATR-FTIR (neat): 2906, 2833, 2360, 2341, 1697, 1415, 1364, 1286, 1170, 1108, 986, 866, 769, 668. HRMS (ESI) m/z (M+Na)$^+$ calculated for C$_{20}$H$_{33}$O$_2$Na: 342.2409 observed: 342.2405.

Tert-butyl 4-(4,8-dimethylnona-3,7-dien-1-yl)-3,6-dihydropyridine-1(2H)-carboxylate (3o): The general procedure A was followed using 75 mg of diene (0.5 mmol, 1.0 equiv) and 241 mg of enol nonaflate (0.5 mmol, 1.0 equiv). The product was then purified by flash column chromatography (2% EtOAc:hexanes) to afford 3o as a colorless oil (85 mg, 51% yield, 1.8:1), $R_f = 0.39$ (10% EtOAc:hexanes). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.34-5.30 (m, 1H), 5.10-5.08 (m, 2H), 3.84 (m, 2H), 3.47 (t, $J = 5.0$ Hz, 2H), 2.65 (m, 2H, minor), 2.10-1.91 (m, 10H), 1.67 (s, 3H), 1.59 (s, 6H), 1.46 (s, 9H), 1.28 (q, $J = 6.7$ Hz, 2H, minor), 0.97 (d, $J = 5.0$ Hz, 3H, minor); $^{13}$C NMR (126 MHz, CDCl$_3$, 50 °C) $\delta$ 155.2, 138.9, 136.8, 135.8, 135.6, 131.7, 131.4, 131.3, 125.5, 125.0, 124.9, 124.6, 124.1, 118.2, 79.5, 43.6, 40.6, 40.0, 37.8, 37.5, 36.6, 32.3, 28.8, 27.1, 26.9, 26.3, 26.2, 26.1, 25.9, 25.8, 23.5, 21.0, 17.9, 16.2; ATR-FTIR (neat): 2972, 2927, 2360, 2342, 1700, 1417, 1352, 1242, 1165, 1141, 968, 861, 768, 668; HRMS (ESI) m/z (M+Na)$^+$ calculated for C$_{21}$H$_{35}$O$_2$Na: 356.2565 observed: 356.2564.

General procedure for the optimization of 1,2-hydrovinylation of 1,3-dienes with $\beta$-keto ester derived enol triflates: The general procedure B described below was used with the following modifications. The reaction was performed on 0.20 mmol scale with $\approx$ 10 wt% internal standard (2-methoxynapthalene). After work-up, the reaction mixture was analyzed for product formation by $^1$HNMR. The modifications described below were applied in order to optimize the reaction.
General procedure B for 1,2-hydrovinylation of 1,3-dienes with β-keto ester derived enol triflates: The general procedure A was followed except 1.3 equiv of enol triflate (0.65 mmol) and 26 mg of Pd$_2$dba$_3$·CHCl$_3$ (0.025 mmol, 0.05 equiv) were used.

**Ethyl (2Z,6E)-7-(4-hydroxyphenyl)-2,3-dimethylhepta-2,6-dienoate (3p):** The general procedure B was followed using 73 mg of diene (0.5 mmol, 1.0 equiv) and 180 mg of enol triflate (0.65 mmol, 1.3 equiv). The product was then purified by flash column chromatography (8→12% EtOAc:hexanes) to afford 3p as a colorless oil (93 mg, 68% yield, 17:1), $R_f$ = 0.16 (10% EtOAc:hexanes). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.20 (d, $J$ = 10.0 Hz, 2H), 6.76 (d, $J$ = 10.0 Hz, 2H), 6.32 (d, $J$ = 15.0 Hz, 1H), 6.06 (td, $J$ = 15.0, 7.5 Hz, 1H), 5.01 (br, 1H), 4.18 (q, $J$ = 6.7 Hz, 2H), 2.51 (t, $J$ = 7.5 Hz, 2H), 2.34 (q, $J$ = 6.7 Hz, 2H), 1.86 (s, 3H), 1.82 (s, 3H), 1.29 (t, $J$ = 7.5 Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 170.1, 154.9, 145.8, 131.0, 129.5, 128.3, 127.5, 123.6, 115.6, 60.4, 36.6, 32.1, 20.6, 16.1, 14.5; ATR-FTIR (neat); 3382, 2979, 2927, 2359, 1681, 1610, 1512, 1443, 1366, 1271, 1168, 1094, 1022, 964, 837, 773. HRMS (ESI) m/z (M+Na)$^+$ calculated for C$_{17}$H$_{22}$O$_3$Na: 297.1467 observed: 297.1471.

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**Table:**

| entry | X   | Y   | % conv. 1d | % yield (3p/4p)$^a$ |
|-------|-----|-----|------------|---------------------|
| 1     | 1.0 | 2   | 80         | 45 (>20:1)          |
| 2     | 1.3 | 2   | 83         | 55 (>20:1)          |
| 3     | 1.3 | 5   | 95         | 68 (17:1)           |

*a) Determined by NMR using an internal standard on 0.2 mmol scale. Yields are a combination of both 3p and 4p.
Ethyl (2Z,6E)-2-(3-(1,3-dioxoisindolin-2-yl)propyl)-7-(4-hydroxyphenyl)-3-methylhepta-2,6-dienoate (3q): The general procedure B was followed using 44 mg of diene (0.3 mmol, 1.0 equiv), 175 mg of enol triflate (0.39 mmol, 1.3 equiv), 31 mg of sodium formate (0.45 mmol, 1.5 equiv), 16 mg of \( \text{Pd}_2 \text{dba}_3 \cdot \text{CHCl}_3 \) (0.015 mmol, 0.05 equiv) and 0.9 mL of DMA. The product was then purified by flash column chromatography (20→30% EtOAc:hexanes) to afford 3q as a colorless oil (83 mg, 64% yield, 20:1), \( R_f = 0.17 \) (30% EtOAc:hexanes). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.83 (dd, \( J = 7.5, 2.5 \) Hz, 2H), 7.70 (d, \( J = 5.0 \) Hz, 2H), 7.15 (d, \( J = 10.0 \) Hz, 2H), 6.74 (d, \( J = 5.0 \) Hz, 2H), 6.26 (d, \( J = 20.0 \) Hz, 1H), 6.04-5.97 (m, 2H), 4.14 (q, \( J = 6.7 \) Hz, 2H), 3.68 (t, \( J = 7.5 \) Hz, 2H), 2.44 (t, \( J = 7.5 \) Hz, 2H), 2.35 (t, \( J = 7.5 \) Hz, 2H), 2.29 (q, \( J = 8.3 \) Hz, 2H), 1.80-1.75 (m, 5H), 1.22 (t, \( J = 5.0 \) Hz, 3H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 169.6, 168.6, 155.2, 146.2, 134.1, 132.2, 130.5, 129.6, 127.5, 127.5, 127.4, 123.4, 115.5, 60.5, 38.1, 36.6, 32.0, 27.8, 27.7, 20.1, 14.4; ATR-FTIR (neat); 3380, 2965, 2930, 2360, 2342, 1716, 1684, 1653, 1559, 1540, 1507, 1457, 669, 650. HRMS (ESI) m/z (M+Na)\(^+\) calculated for C\(_{27}\)H\(_{29}\)NO\(_5\)Na: 470.1943 observed: 470.1939.

Ethyl (2E,6E)-7-(4-hydroxyphenyl)-2-methyl-3-(2-(trimethylsilyl)ethyl)hepta-2,6-dienoate (3r): The general procedure B was followed using 73 mg of diene (0.5 mmol, 1.0 equiv) and 236 mg of enol triflate (0.65 mmol, 1.3 equiv). The product was then purified by flash column chromatography (6→12% EtOAc:hexanes) to afford 3r as a colorless oil (112 mg, 62% yield, 10.2:1), \( R_f = 0.18 \) (10% EtOAc:hexanes). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.20 (d, \( J = 10.0 \) Hz, 2H), 6.77 (d, \( J = 5.0 \) Hz, 2H), 6.32 (d, \( J = 19.5 \) Hz, 1H), 6.07 (td, \( J = 15.0, 7.5 \) Hz, 1H), 5.11 (s, 1H), 4.18 (q, \( J = 6.7 \) Hz, 2H), 2.50 (t, \( J = 7.5 \) Hz, 2H), 2.32 (q, \( J = 6.7 \) Hz, 2H), 2.11-2.07 (m, 2H), 1.86 (s, 3H), 1.29 (t, \( J = 7.5 \) Hz, 3H), 0.65-0.61 (m, 2H), -0.03 (s, 9H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 170.3, 154.9, 153.0, 131.0, 129.4, 128.5, 127.5, 127.5, 122.2, 115.6, 60.4, 34.1, 32.5, 28.1, 15.4, 15.1, 14.5, -1.7; ATR-FTIR (neat); 3390, 2950, 2360, 2342, 1717, 1653, 1510, 1460, 1246, 1170, 1093, 1035, 840, 760, 694, 668. HRMS (ESI) m/z (M+Na)\(^+\) calculated for C\(_{22}\)H\(_{32}\)O\(_3\)SiNa: 383.2018 observed: 383.2021.
Ethyl (2Z,6E)-2-benzyl-7-(4-methoxyphenyl)-3-methylhepta-2,6-dienoate (3s): The general procedure B was followed using 80 mg of diene (0.5 mmol, 1.0 equiv) and 229 mg of enol nonaflate (0.65 mmol, 1.3 equiv). The product was then purified by flash column chromatography (3→6% EtOAc:hexanes) to afford 3s as a colorless oil (91 mg, 50% yield, 9.4:1), $R_f = 0.38$ (10% EtOAc:hexanes). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.27 (d, $J = 10.0$ Hz, 2H), 7.21-7.14 (m, 5H), 6.84 (d, $J = 10.0$ Hz, 2H), 6.36 (d, $J = 15.0$ Hz, 1H), 6.13 (td, $J = 16.7$, 5.0 Hz, 1H), 4.10 (q, $J = 8.3$ Hz, 2H), 3.81 (s, 3H), 3.70 (s, 2H), 2.59 (t, $J = 7.5$ Hz, 2H), 2.43 (q, $J = 6.7$ Hz, 2H), 1.88 (s, 3H), 1.16 (t, $J = 7.5$ Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 169.2, 158.9, 147.2, 139.9, 130.8, 129.7, 128.5, 128.3, 128.2, 127.6, 127.3, 126.1, 114.1, 60.4, 55.5, 36.5, 35.9, 32.1, 20.5, 14.4; ATR-FTIR (neat); 2926, 2360, 2342, 1709, 1607, 1540, 1437, 1361, 1247, 1176, 1085, 1032, 967, 846, 735, 700, 668. HRMS (ESI) m/z (M+Na)$^+$ calculated for C$_{24}$H$_{28}$O$_3$Na: 387.1936 observed: 387.1935.

Through-space $^1$H–$^1$H interactions present within 3s were obtained using a 1D nOe NMR experiment in CDCl$_3$ (500 MHz). The benzyl peak at 3.70 ppm was irradiated and a substantial nOe was observed at the the methyl protons (1.87 ppm). This result assigns the Z-configuration of tetrasubstituted alkene in 3s.

Ethyl (2E,6E)-7-(4-hydroxyphenyl)-3-methyl-2-((trimethylsilyl)methyl)hepta-2,6-dienoate (3t): The general procedure B was followed using 73 mg of diene (0.5 mmol, 1.0 equiv) and 226 mg of enol triflate (0.65 mmol, 1.3 equiv). The product was then purified by flash column chromatography (6→12% EtOAc:hexanes) to afford 3t as a colorless oil (47 mg, 27% yield, 10.3:1), $R_f = 0.18$ (10% EtOAc:hexanes). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.20 (d, $J = 8.0$ Hz, 2H), 6.76 (d, $J = 12.0$ Hz, 2H), 6.31 (d, $J = 16.0$ Hz, 1H), 6.08 (td, $J = 16.0$, 8.0 Hz, 1H), 4.98 (br, 1H), 4.16 (q, $J = 8.0$ Hz, 2H), 2.45 (t, $J = 6.0$ Hz, 2H), 2.35 (q, $J = 6.7$ Hz, 2H), 1.81 (s, 2H), 1.74 (s, 3H), 1.29 (t, $J = 6.0$ Hz, 3H), -0.01 (s, 9H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 170.3, 154.8, 140.5, 131.1, 129.4, 128.5, 127.4, 126.5, 115.5, 60.4, 36.6, 32.5, 20.7 (20.74), 20.7 (20.65), 14.5, -0.9; ATR-FTIR (neat); 3392, 2953, 2360, 2342, 1708, 1612, 1512, 1445, 1368, 1246, 1169, 1097, 1032, 838, 757, 692, 668. HRMS (ESI) m/z (M+Na)$^+$ calculated for C$_{20}$H$_{36}$O$_3$SiNa: 369.1862 observed: 369.1868.

S20
(Z)-3-((E)-6-phenylhex-5-en-2-ylidene)dihydrofuran-2(3H)-one (3u): The general procedure B was followed using 65 mg of diene (0.5 mmol, 1.0 equiv) and 169 mg of enol triflate (0.65 mmol, 1.3 equiv). The product was then purified by flash column chromatography (6→10% EtOAc:hexanes) to afford 3u as a colorless oil (70 mg, 58% yield, 11.6:1), Rf = 0.50 (25% EtOAc:hexanes). 1H NMR (500 MHz, CDCl3) δ 7.33-7.27 (m, 4H), 7.19 (t, J = 7.5 Hz, 1H), 6.40 (d, J = 15.0 Hz, 1H), 6.25 (td, J = 15.0, 5.0 Hz, 1H), 4.28 (t, J = 7.5 Hz, 2H), 2.95 (t, J = 7.5 Hz, 2H), 2.86 (t, J = 7.5 Hz, 2H), 2.39 (q, J = 6.7 Hz, 2H), 1.90 (t, J = 1.5 Hz, 3H); 13C NMR (126 MHz, CDCl3) δ 170.3, 153.6, 137.8, 130.6, 130.0, 128.7, 126.2, 119.3, 64.4, 32.6, 32.0, 30.0, 22.8; ATR-FTIR (neat); 3024, 2919, 2854, 2360, 2342, 1735, 1654, 1550, 1521, 1447, 1374, 1264, 1195, 1162, 1061, 1035, 966, 744, 694, 668, 655. HRMS (ESI) m/z calculated for C16H18O2Na: 265.1204 observed: 265.1201.

Ethyl (2E,6E)-7-(4-hydroxyphenyl)-2,3-dimethylhepta-2,6-dienoate (3v): The general procedure B was followed using 73 mg of diene (0.5 mmol, 1.0 equiv) and 180 mg of enol triflate (0.65 mmol, 1.3 equiv). The product was then purified by flash column chromatography (5→10% EtOAc:hexanes) to afford 3v as a colorless oil (82 mg, 60% yield, 3v:4v::>20:1, 3v:3p::6.6:1), Rf = 0.16 (10% EtOAc:hexanes). 1H NMR (400 MHz, CDCl3) δ 7.21 (d, J = 8.0 Hz, 2H), 6.77 (d, J = 8.0 Hz, 2H), 6.34 (d, J = 16.0 Hz, 1H), 6.09-6.02 (m, 1H), 5.46 (br, 1H), 4.20 (q, J = 8.0 Hz, 2H), 2.50 (t, J = 8.0 Hz, 2H, minor), 2.34 (q, J = 6.0 Hz, 2H, minor), 2.29 (br, 4H), 2.02 (d, J = 1.2 Hz, 3H), 1.89 (d, J = 1.6 Hz, 3H), 1.86 (s, 3H, minor), 1.82 (s, 3H, minor), 1.31 (t, J = 6.0 Hz, 3H). 13C NMR (126 MHz, CDCl3) major δ 170.3, 155.1, 145.6, 130.8, 130.0, 127.7, 127.5, 123.5, 115.6, 60.4, 36.3, 31.0, 21.2, 15.6, 14.5; Minor δ 170.1, 154.9, 145.7, 131.0, 129.5, 128.3, 127.5, 123.6, 115.6, 60.4 (overlapping), 36.6, 32.1, 20.6, 16.1, 14.5; ATR-FTIR (neat); 3382, 2979, 2927, 2359, 1681, 1610, 1512, 1443, 1366, 1271, 1168, 1094, 1022, 964, 837, 773. HRMS (ESI) m/z (M+Na)+ calculated for C17H22O3Na: 297.1467 observed: 297.1471.
Through-space $^1$H–$^1$H interactions present within $3v$ were obtained using a 1D nOe NMR experiment in CDCl$_3$ (500 MHz). The methyl peak at 2.02 ppm was irradiated and no substantial nOe was observed upon the other methyl protons (1.89 ppm). This result, and comparison of the $^1$HNMR of $3p$ and $3v$, assigns the $E$-configuration of tetrasubstituted alkene in $3v$.

(2E,6E)-2,3-dimethyl-7-phenylhepta-2,6-dien-1-ol ($3w$): The general procedure B was followed using 83 mg of diene (0.64 mmol, 1.0 equiv), 195 mg of enol triflate (0.83 mmol, 1.3 equiv), 65 mg of sodium formate (0.96 mmol, 1.5 equiv), 33 mg of Pd$_2$dba$_3$·CHCl$_3$ (0.015 mmol, 0.05 equiv) and 2.0 mL of DMA. The product was then purified by flash column chromatography (8→12% EtOAc:hexanes) to afford $3w$ as a colorless oil (92 mg, 66% yield, 9.6:1), $R_f$ = 0.12 (10% EtOAc:hexanes). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.35-7.28 (m, 4H), 7.20 (t, $J$ = 7.5 Hz, 1H), 6.41 (d, $J$ = 15.0 Hz, 1H), 6.23 (td, $J$ = 15.0, 7.5 Hz, 1H), 4.14 (s, 2H), 2.31 (q, $J$ = 6.7 Hz, 2H), 2.24 (t, $J$ = 7.5 Hz, 2H), 1.79 (s, 3H), 1.78 (s, 3H), 1.29 (br, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 137.9, 132.5, 130.5, 130.2, 128.7, 127.1, 126.1, 64.2, 34.9, 31.5, 18.2, 16.5; ATR-FTIR (neat); 3327, 3024, 2921, 2860, 1494, 1446, 1372, 1239, 1071, 994, 961, 741, 714, 694. HRMS (ESI) m/z (M+Na)$^+$ calculated for C$_{15}$H$_{20}$ONa: 239.1412 observed: 239.1413.
Through-space $^1$H–$^1$H interactions present within $3w$ were obtained using a 1D nOe NMR experiment in CDCl$_3$ (500 MHz). The allylic peak at 4.14 ppm was irradiated and a substantial nOe was observed at the methyl protons (1.78 and 1.79 ppm, Fig. 1). However, the allylic protons at 2.24 ppm were unaffected. Similarly, the irradiation of allylic peak at 2.24 ppm lead to a substantial nOe of methyl protons (1.78 and 1.79 ppm), whereas allylic protons at 4.14 ppm remained unaffected (Fig. 2). This result, and comparison of the $^1$HNMR of $3w$ and $3x$, assigns the $E$-configuration of tetrasubstituted alkene in $3w$.

(2Z,6E)-2,3-dimethyl-7-phenylhepta-2,6-dien-1-ol ($3x$): The general procedure B was followed using 65 mg of diene (0.5 mmol, 1.0 equiv) and 152 mg of enol triflate (0.65 mmol, 1.3 equiv). The product was then purified by flash column chromatography (8→12% EtOAc:hexanes) to afford $3x$ as a colorless oil (73 mg, 67% yield, 9:1), $R_f = 0.18$ (10% EtOAc:hexanes). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.34-7.27 (m, 4H), 7.19 (t, $J = 7.5$ Hz, 1H), 6.38 (d, $J = 15.0$ Hz, 1H), 6.22-6.16 (m, 1H), 4.12 (s, 2H), 2.29 (s, 4H), 1.76 (s, 3H), 1.73 (s, 3H), 1.10 (br, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 137.8, 132.6, 130.6, 130.4, 128.9, 128.8, 127.2, 126.1, 63.8, 34.2, 32.5, 19.1, 16.9; ATR-FTIR (neat): 3329, 3024, 2921, 2860, 2360, 2342, 1495, 1447, 1373, 995, 962, 742, 714, 693, 668. HRMS (ESI) m/z calculated for $C_{15}H_{20}ONa$: 239.1412 observed: 239.1413.

Through-space $^1$H–$^1$H interactions present within $3x$ were obtained using a 1D nOe NMR experiment in CDCl$_3$ (500 MHz). The allylic peak at 4.12 ppm was irradiated and a substantial nOe was observed upon the other allylic protons (1.76 and 2.29 ppm). This result, and comparison of the $^1$HNMR of $3w$ and $3x$, assigns the Z-configuration of tetrasubstituted alkene in $3x$. 
Ethyl \( (2E,6E) \)-7-(4-methoxyphenyl)-3-methylhepta-2,6-dienoate (3y): The general procedure B was followed using 80 mg of diene (0.5 mmol, 1.0 equiv) and 170 mg of enol triflate (0.65 mmol, 1.3 equiv). The product was then purified by flash column chromatography (6→10% EtOAc:hexanes) to afford 3y as a colorless oil (77 mg, 56% yield, 13:1), \( R_f = 0.42 \) (20% EtOAc:hexanes). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \): 7.26 (d, \( J = 10.0 \) Hz, 2H), 6.84 (d, \( J = 10.0 \) Hz, 2H), 6.36 (d, \( J = 15.0 \) Hz, 1H), 6.03 (td, \( J = 15.0, 7.5 \) Hz, 1H), 5.71 (s, 1H), 4.15 (q, \( J = 6.7 \) Hz, 2H), 3.80 (s, 3H), 2.38 (q, \( J = 6.7 \) Hz, 2H), 2.30 (t, \( J = 7.5 \) Hz, 2H), 2.19 (d, \( J = 1.5 \) Hz, 3H), 1.28 (t, \( J = 7.5 \) Hz, 3H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \): 167.0, 159.3, 159.0, 130.5, 130.2, 127.3, 127.1, 116.2, 114.1, 59.8, 55.4, 41.0, 31.1, 19.1, 14.6; ATR-FTIR (neat); 2940, 2360, 2342, 1734, 1717, 1700, 1653, 1559, 1540, 1521, 1457, 668, 655. HRMS (ESI) m/z (M+Na\(^+\)) calculated for C\(_{17}\)H\(_{22}\)O\(_3\)Na: 297.1467 observed: 297.1469.

Dimethyl \((1E,5E)\)-6-(4-methoxyphenyl)-2-methylhexa-1,5-dien-1-ylphosphonate (3z): The general procedure B was followed using 80 mg of diene (0.5 mmol, 1.0 equiv) and 194 mg of enol triflate (0.65 mmol, 1.3 equiv). The product was then purified by flash column chromatography (70→90% EtOAc:hexanes) to afford 3z as a colorless oil (98 mg, 63% yield, 12:1), \( R_f = 0.17 \) (70% EtOAc:hexanes). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \): 7.25 (d, \( J = 10.0 \) Hz, 2H), 6.83 (d, \( J = 10.0 \) Hz, 2H), 6.35 (d, \( J = 15.0 \) Hz, 1H), 6.01 (td, \( J = 16.7, 7.5 \) Hz, 1H), 5.39 (d, \( J = 20.0 \) Hz, 1H), 3.80 (s, 3H), 3.68 (s, 3H), 3.66 (s, 3H), 2.40-2.31 (m, 4H), 2.12 (d, \( J = 5.0 \) Hz, 3H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \): 163.5, 159.0, 130.4, 127.3, 126.8, 114.1, 111.5, 109.9, 55.5, 52.2, 41.6, 41.4, 31.0, 20.5; ATR-FTIR (neat); 2940, 2360, 2342, 1707, 1653, 1510, 1457, 1419, 1362, 1243, 1175, 1026, 829, 669, 572. HRMS (ESI) m/z (M+Na\(^+\)) calculated for C\(_{16}\)H\(_{23}\)O\(_4\)PNa: 333.1232 observed: 333.1227.

Ethyl \((2Z,6E)\)-7-(4-hydroxyphenyl)-3-(2-(trimethylsilyl)ethyl)hepta-2,6-dienoate (3ab): The general procedure B was followed using 44 mg of diene (0.3 mmol, 1.0 equiv), 136 mg of enol triflate (0.39
mmol, 1.3 equiv), 31.0 mg of sodium formate (0.45 mmol, 1.5 equiv), 16 mg of Pd$_2$dba$_3$·CHCl$_3$ (0.015 mmol, 0.05 equiv) and 0.9 mL of DMA. The product was then purified by flash column chromatography (8→12% EtOAc:hexanes) to afford 3ab as a colorless oil (67 mg, 67% yield, 9.4:1), R$_f$ = 0.13 (10% EtOAc:hexanes). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.22 (d, J = 9.0 Hz, 2H), 6.77 (d, J = 9.0 Hz, 2H), 6.35 (d, J = 15.0 Hz, 1H), 6.04 (td, J = 14.0, 6.0 Hz, 1H), 5.61 (s, 1H), 5.08 (br, 1H), 4.15 (q, J = 8.0 Hz, 2H), 2.61-2.56 (m, 2H), 2.37-2.29 (m, 4H), 1.28 (t, J = 7.5 Hz, 3H), 0.71-0.65 (m, 2H), 0.04 (s, 9H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 166.9, 166.4, 155.1, 130.6, 130.1, 137.5, 127.2, 115.6, 114.4, 59.8, 37.3, 31.3, 26.5, 16.1, 14.6, -1.6; ATR-FTIR (neat): 3330, 2920, 2359, 2342, 1717, 1700, 1684, 1653, 1647, 1507, 1541, 1521, 1457, 1468, 165. HRMS (ESI) m/z (M+Na)$^+$ calculated for C$_{20}$H$_{30}$O$_3$SiNa: 369.1862 observed: 369.1866.

Procedure for scale up:

Ethyl (2Z,6E)-7-(4-((I1-oxidanyl)-l15-methyl)-3-hydroxyphenyl)-2,3-dimethylhepta-2,6-dienoate (3p): To a 20 mL oven dried vial with a stir bar was added 1.2 g of diene 1c (7.0 mmol, 1.0 equiv), 2.5 g of enol triflate 2p (9.1 mmol, 1.3 equiv), 714 mg of sodium formate (10.5 mmol, 1.5 equiv), 362 mg of Pd$_2$dba$_3$·CHCl$_3$ (0.35 mmol, 0.05 equiv) and 7.0 mL of DMA. The vial was sealed under nitrogen atmosphere with a phenolic screw cap. Further, parafilm was wrapped around the cap to make the vial air tight. The suspension was then allowed to stir at room temperature for 16 h followed by filtration through a plug of silica gel with 20 mL of methy tert-butyl ether (MTBE). The solution was transferred to a separatory funnel and further diluted with 100 mL of MTBE and washed with 3x25 mL of water and finally with brine (1x25 mL). The organic layer was dried over anhydrous MgSO$_4$ followed by removal of solvents under reduced pressure. The $^1$H NMR of the crude reaction mixture was taken at this stage to determine the reported regio-selectivity of the reduction. The product was then purified by flash column chromatography (6→10% EtOAc:hexanes) to afford 3p as a yellow oil (1.6 g, 75% yield, 3p:4p::16:1), R$_f$ = 0.12 (10% EtOAc:hexanes). Note: Yields are reported as a mixture of isomers. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 6.96 (s, 1H), 6.78 (q, J = 8.3 Hz, 2H), 6.29 (d, J = 15.0 Hz, 1H), 6.08 (td, J = 12.5, 6.3 Hz, 1H), 5.69 (d, J = 4.0 Hz, 1H), 4.18 (q, J = 6.7 Hz, 2H), 3.85 (s, 3H), 2.50 (t, J = 7.5 Hz, 2H), 2.34 (q, J = 6.7 Hz, 2H), 1.86 (s, 3H), 1.81 (s, 3H), 1.29 (t, J = 7.5 Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 169.8, 145.9, 145.8, 145.5, 131.8, 129.5, 128.8, 132.6, 118.4, 111.8, 110.7, 60.3, 56.1, 36.5, 32.1, 20.5, 16.0, 14.5; ATR-FTIR (neat):
3430, 2934, 2840, 1701, 1584, 1509, 1440, 1267, 1211, 1162, 1094, 1026, 963, 869, 760, 609; HRMS (ESI) m/z (M+Na)$^+$ calculated for $C_{18}H_{26}O_4$Na: 327.1572 observed: 327.1570.

**Procedure for the selective reduction of $3p'$:**

![Reduction Reaction Diagram]

**Ethyl (Z)-7-(4-((l1-oxidanyl)-l5-methyl)-3-hydroxyphenyl)-2,3-dimethylhept-2-enoate ($3p'$-red):** To a 20 mL oven dried Schlenk flask with a stir bar was added 100 mg of $3p'$ (0.33 mmol, 1.0 equiv), 0.9 mg of 10 wt. % Pd on activated carbon (0.008 mmol, 0.025 equiv). The flask was connected to a three way adapter fitted with a hydrogen balloon on one end. The flask was evacuated and filled with hydrogen and the process was repeated three times. The suspension was then allowed to stir at room temperature for 30 min followed by filtration through a plug of silica gel with 10 mL of methy tert-butyl ether (MTBE). The solvents were evaporated under reduced pressure to afford $3p'$-red as a colorless oil (100 mg, 99% yield). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 6.75 (d, $J = 10.0$ Hz, 2H), 6.64 (dd, $J = 8.5, 2.0$ Hz, 1H), 5.68 (s, 1H), 4.17 (q, $J = 6.7$ Hz, 2H), 3.84 (s, 3H), 2.53 (t, $J = 7.5$ Hz, 2H), 2.36 (t, $J = 7.5$ Hz, 2H), 1.84 (s, 3H), 1.75 (d, $J = 1.0$ Hz, 3H), 1.59 (quint, $J = 7.5$ Hz, 2H), 1.48 (quint, $J = 7.5$ Hz, 2H), 1.28 (t, $J = 7.5$ Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 170.0, 146.2, 145.6, 144.8, 136.2, 123.0, 119.8, 114.8, 110.7, 60.2, 56.1, 36.3, 35.3, 31.7, 28.1, 20.2, 16.0, 14.4; ATR-FTIR (neat): 3447, 2932, 2857, 2360, 2342, 1700, 1590, 1509, 1442, 1270, 1208, 1091, 1027, 799, 760, 736, 668; HRMS (ESI) m/z (M+Na)$^+$ calculated for $C_{18}H_{26}O_4$Na: 329.1729 observed: 329.1733.
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| f1 (ppm) | Value     |
|---------|-----------|
|         | -1.63     |
|         | 14.58     |
|         | 16.09     |
|         | 26.47     |
|         | 31.30     |
|         | 37.73     |
|         | 59.84     |
|         | 76.98     |
|         | 77.23     |
|         | 77.48     |
|         | 114.41    |
|         | 115.61    |
|         | 127.24    |
|         | 127.48    |
|         | 130.13    |
|         | 130.56    |
|         | 155.09    |
|         | 166.43    |
|         | 166.93    |
