Cu-catalyzed highly selective reductive functionalization of 1,3-diene using H$_2$O as stoichiometric hydrogen atom donor

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1. General Considerations

All manipulations were conducted with Schlenk tube. $^1$H-NMR spectra were recorded on Bruker AVIII-400 spectrometers. Chemical shifts (in ppm) were referenced to tetramethylsilane ($\delta = 0$ ppm) in CDCl$_3$ as an internal standard. $^{13}$C-NMR spectra were obtained by using the same NMR spectrometers and were calibrated with CDCl$_3$ ($\delta = 77.00$ ppm). $^{19}$F-NMR spectra were obtained by the same NMR and CF$_3$COOH was employed as external standard for the $^{19}$F-NMR measurement. IR spectra were recorded using a Bruker ALPHA. High resolution mass spectrometry (HRMS) data were obtained on a QTOF mass analyzer with electrospray ionization (ESI) through a Bruker Daltonicmior OTOF-QII. Dry 1,2-dichloroethanewas purchased from Energy Chemical. Substrates were purchased from Aldrich, TCI, Acros, Energy, Aladdin, or synthesized according to the procedures outlined below. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.
2. Synthesis of Diene Substrates

These substrates were prepared according to the corresponding literature reports. Analytical data (\(^1\)H NMR, \(^{13}\)C NMR) matches with the corresponding literature.

1a: \((E)\)-buta-1,3-dien-1-ylbenzene\(^1\)

1a-mix: buta-1,3-dien-1-ylbenzene\(^2\)

1b: \((E)\)-1-(buta-1,3-dien-1-yl)-2-methylbenzene\(^1\)

1c: \((E)\)-1-(buta-1,3-dien-1-yl)-3-methylbenzene\(^1\)

1d: \((E)\)-1-(buta-1,3-dien-1-yl)-4-methylbenzene\(^1\)

1e: \((E)\)-1-(buta-1,3-dien-1-yl)-4-methoxybenzene\(^1\)

1f: \((E)\)-4-(buta-1,3-dien-1-yl)-N,N-dimethylaniline\(^3\)

1g: \((E)\)-1-(buta-1,3-dien-1-yl)-4-fluorobenzene\(^3\)

1h: \((E)\)-1-(buta-1,3-dien-1-yl)-4-(trifluoromethyl)benzene\(^4\)

1i: \((E)\)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene\(^1\)

1j: \((E)\)-1-bromo-4-(buta-1,3-dien-1-yl)benzene\(^5\)

1k: \((E)\)-2-(buta-1,3-dien-1-yl)naphthalene\(^1\)

1m: \((E)\)-2-(buta-1,3-dien-1-yl)furan\(^1\)

1n: \((E)\)-3-(buta-1,3-dien-1-yl)thiophene\(^5\)

1o: \((E)\)-hexa-3,5-dien-1-ylbenzene\(^1\)

1p: \((E)\)-nona-1,3-diene\(^6\)

1q: \((E)\)-buta-1,3-dien-1-ylcyclohexane\(^1\)

1r: \((1R,5S)\)-6,6-dimethyl-2-vinylbicyclo[3.1.1]hept-2-ene\(^7\)
Preparation of (E)-1-(buta-1,3-dien-1-yl)-4-iodobenzene (1k):
A suspension of methyltriphenylphosphonium bromide (2.9 g, 8.1 mmol) in dry THF (30 ml) was cooled at 0°C with an ice bath under inert atmosphere. Then n-BuLi (3.2 ml, 2.5 M in n-hexane, 8.1 mmol) was added dropwise. After stirring for 30 min, the solution of (E)-3-(4-iodophenyl)acrylaldehyde (1.4 g, 5.4 mmol) in THF (20 ml) was added dropwise. Then the reaction mixture was warmed to room temperature for one hour. Then the reaction mixture was quenched with sat. NH₄Cl aq. (20 mL), and extracted by EtOAc (20 mL × 3). The combined organic layers were dried over MgSO₄ and concentrated in vacuo. The residue was purified by silica-gel column chromatography to give the yellow solid 1k (0.89 g, 64%).
3. The effect of different reaction conditions

Table S1. The effect of different base \(^{a}\)

![Chemical reaction diagram]

<table>
<thead>
<tr>
<th>entry</th>
<th>base</th>
<th>yield (%)(^{b})</th>
<th>dr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LiO(^t)Bu</td>
<td>76</td>
<td>5:1</td>
</tr>
<tr>
<td>2</td>
<td>NaO(^t)Bu</td>
<td>52</td>
<td>4:1</td>
</tr>
<tr>
<td>3</td>
<td>KO(^t)Bu</td>
<td>69</td>
<td>5:1</td>
</tr>
<tr>
<td>4</td>
<td>LiOH</td>
<td>63</td>
<td>1:1</td>
</tr>
<tr>
<td>5</td>
<td>LiOMe</td>
<td>66</td>
<td>2:1</td>
</tr>
<tr>
<td>6</td>
<td>Li(_2)CO(_3)</td>
<td>70</td>
<td>4:1</td>
</tr>
<tr>
<td>7</td>
<td>Na(_2)CO(_3)</td>
<td>64</td>
<td>3:1</td>
</tr>
<tr>
<td>8</td>
<td>KOEt</td>
<td>89</td>
<td>1:1</td>
</tr>
<tr>
<td>9</td>
<td>KOAc</td>
<td>30</td>
<td>5:1</td>
</tr>
</tbody>
</table>

\(^{a}\) 1a (0.25 mmol), 2a (0.5 mmol), B\(_2\)Pin\(_2\) (0.5 mmol), base (0.5 mmol), Cu(OTf)\(_2\) (10 mol%), PPh\(_3\) (11 mol%), H\(_2\)O (3.0 equiv), THF (1.5 ml). \(^{b}\) Isolated yield of both diastereomers, dr was determined by \(^1\)H-NMR.
Table S2. The effect of different solvent $^a$

<table>
<thead>
<tr>
<th>entry</th>
<th>solvent</th>
<th>yield (%)$^b$</th>
<th>dr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,4-dioxane</td>
<td>64</td>
<td>4:1</td>
</tr>
<tr>
<td>2</td>
<td>toluene</td>
<td>80</td>
<td>9:1</td>
</tr>
<tr>
<td>3</td>
<td>DMA</td>
<td>64</td>
<td>1:1</td>
</tr>
<tr>
<td>4</td>
<td>DCE</td>
<td>93</td>
<td>&gt;20:1</td>
</tr>
<tr>
<td>5</td>
<td>CHCl$_3$</td>
<td>58</td>
<td>10:1</td>
</tr>
<tr>
<td>6</td>
<td>DMSO</td>
<td>58</td>
<td>3:1</td>
</tr>
<tr>
<td>7</td>
<td>Ph-Cl</td>
<td>89</td>
<td>15:1</td>
</tr>
<tr>
<td>8</td>
<td>isopropanol</td>
<td>81</td>
<td>2:1</td>
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</table>

$^a$ 1a (0.25 mmol), 2a (0.5 mmol), B$_2$Pin$_2$ (0.5 mmol), LiO$_t$-Bu (0.5 mmol), Cu(OTf)$_2$ (10 mol%), PPh$_3$ (11 mol%), H$_2$O (3.0 equiv), solvent (1.5 ml). $^b$ Isolated yield of both diastereomers, dr was determined by $^1$H-NMR.
Table S3. The effect of different catalyst.\(^a\)

\[
\begin{align*}
\text{entry} & & \text{solvent} & & \text{yield (\%)\(^b\)} & & \text{dr} \\
1 & & \text{Cu(acac)}_{2} & & 76 & & >20:1 \\
2 & & \text{CuCl} & & 78 & & >20:1 \\
3 & & \text{CuBr} & & 88 & & >20:1 \\
4 & & \text{CuOAc} & & 23 & & 13:1 \\
5 & & \text{Cu(OH)}_{2} & & 14 & & 11:1 \\
6 & & \text{CuI} & & 74 & & >20:1 \\
\end{align*}
\]

\(^{a}\) 1a (0.25 mmol), 2a (0.5 mmol), B\(_{2}\)Pin\(_{2}\) (0.5 mmol), LiO\(^{t}\)Bu (0.5 mmol), cat. (10 mol%), PPh\(_{3}\) (11 mol%), H\(_{2}\)O (3.0 equiv), DCE (1.5 mL). \(^{b}\) Isolated yield of both diastereomers, dr was determined by \(^{1}\)H-NMR.
Table S4. The effect of different ligand $^{a, b}$

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{Cu(OTf)}_2 (10 \text{ mol%), ligand (11 \text{ mol%})} \\
\text{LiO}^\circ \text{Bu (2.0 equiv), } B_2\text{Pin}_2 (2.0 \text{ equiv}) \\
\text{H}_2\text{O (3.0 equiv), DCE, 70 } ^\circ\text{C, N}_2 \\
\end{align*}
\]

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Yield</th>
<th>DR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph$_2$P$\underline{\text{PPh}}$$_2$</td>
<td>85% (10:1)</td>
<td></td>
</tr>
<tr>
<td>Ph$_2$P$\underline{\text{PPh}}$$_2$</td>
<td>85% (10:1)</td>
<td></td>
</tr>
<tr>
<td>FeP$_2$P$\underline{\text{PPh}}$$_2$</td>
<td>83% (12:1)</td>
<td></td>
</tr>
<tr>
<td>NMe$_2$PCy$_2$</td>
<td>79% (&gt;20:1)</td>
<td></td>
</tr>
<tr>
<td>MeOPOMePCy$_2$</td>
<td>91% (&gt;20:1)</td>
<td></td>
</tr>
<tr>
<td>PPh$_2$PPh$_2$</td>
<td>84% (2:1)</td>
<td></td>
</tr>
<tr>
<td>iPr$iPr$P(tBu)$_2$</td>
<td>70% (9:1)</td>
<td></td>
</tr>
<tr>
<td>iPr$iPr$PCy$_2$</td>
<td>35% (7:1)</td>
<td></td>
</tr>
<tr>
<td>FeP$_2$P$_2$</td>
<td>85% (&gt;20:1)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ 1a (0.25 mmol), 2a (0.5 mmol), B$_2$Pin$_2$ (0.5 mmol), LiO$^\circ$Bu (0.5 mmol), Cu(OTf)$_2$ (10 mol%), ligand (11 mol%), H$_2$O (3.0 equiv), DCE (1.5 ml). $^b$ Isolated yield of both diastereomers, dr were determined by $^1$H-NMR.
4. General procedure for the reaction

General procedure for Cu-catalyzed highly selective reductive functionalization of 1,3-diene:

\[
\begin{align*}
1 & \quad + \quad 2 \\
\xrightarrow{\text{Cu(OTf)}_2, \text{PPh}_3, \text{LiO}^+\text{Bu}, \text{B} \text{Pin}_2, \text{H}_2\text{O}, \text{DCE}, 70^\circ\text{C}, \text{N}_2} & \quad \text{H} \quad \xrightarrow{R} \quad 3
\end{align*}
\]

A stirring bar containing oven dried 25-ml Schlenk tube was charged with Cu(OTf)_2 (9.1 mg, 0.025 mmol, 10 mol%), PPh_3 (7.2 mg, 0.0275 mmol, 11 mol%), B_2Pin_2 (127 mg, 0.50 mmol, 2.0 equiv) and LiO^+Bu (40 mg, 0.50 mmol, 2.0 equiv). The tube was then evacuated and back-filled under a N_2 flow (this sequence was repeated three times). Diene \(1\) (0.25 mmol, 1.0 equiv), water (13.5 \mu L, 3.0 equiv), anhydrous DCE (1.0 ml) were added subsequently under N_2. The reaction mixture was stirred for 1.5 h at r.t. Then the solution of \(2\) (0.50 mmol, 2.0 equiv) in anhydrous DCE (0.5 ml) were added into the reaction system. The reaction was stirred at 70 °C for 24 h. After cooling to r.t, the reaction mixture diluted with EtOAc (10 ml) and H_2O (10 ml). Then it was extracted with EtOAc (10 ml × 3). The organic layer was combined and dried over Na_2SO_4. Then filtered and concentrated by rotary evaporation. The residue was purified by silica gel column chromatography to afford the product \(3\).

Based on the literature *J. Am. Chem. Soc.* 2013, 135, 6026, the configuration of the product \(3\) (racemic) is shown as bellow:

![Configuration of product 3](image)

Procedure for large scale reaction

\[
\begin{align*}
\text{Ph}\text{=CHCH=Ph} & \quad + \quad \text{Ph}\text{=CCH=Ph} \\
\xrightarrow{\text{Cu(OTf)}_2, \text{PPh}_3, \text{LiO}^+\text{Bu}, \text{B} \text{Pin}_2, \text{H}_2\text{O}, \text{DCE}, 70^\circ\text{C}, \text{N}_2} & \quad \text{Ph}\text{=CCH=Ph} \quad \xrightarrow{\text{H} \quad \xrightarrow{\text{R} \quad \text{Ph} \text{=CHCH=Ph}} \quad 3aa
\end{align*}
\]

1.5 g, 11.5 mmol 2.4 g, 23 mmol 75 % yield, ≥20:1 dr, 2g

The general procedure was followed using \(1\) (1.5 g, 11.5 mmol, 1.0 equiv), \(2\) (2.44 g, 23 mmol, 2.0 equiv), Cu(OTf)_2 (416 mg, 1.15 mmol, 10 mol%), PPh_3 (332 mg, 1.27 mmol, 11 mol%), B_2Pin_2 (5.84 g, 23 mmol, 2.0 equiv), LiO^+Bu (1.84 g, 23 mmol, 2.0 equiv), water (0.62 mL, 3.0 equiv), anhydrous DCE (69 ml) to afford \(3\) (2 g, 75%, ≥20:1 dr).
5. Control experiments

5-1. The reaction without aldehyde.

A stirring bar containing oven dried 25-ml Schlenk tube was charged with Cu(OTf)$_2$ (9.1 mg, 0.025 mmol, 10 mol%), PPh$_3$ (7.2 mg, 0.0275 mmol, 11 mol%), B$_2$Pin$_2$ (127 mg, 0.50 mmol, 2.0 equiv) and LiO$^-$Bu (40 mg, 0.50 mmol, 2.0 equiv). The tube was then evacuated and back-filled under a N$_2$ flow (this sequence was repeated three times). Diene 1a (33 mg, 0.25 mmol), water (13.5 μL, 3.0 equiv), anhydrous DCE (1.0 ml) were added subsequently under N$_2$ condition. The reaction mixture was stirred for 1.5 h at room temperature and diluted with EtOAc (10 ml) and H$_2$O (10 ml). Then it was extracted with EtOAc (10 ml × 3). The organic layer was combined and dried over Na$_2$SO$_4$, filtered and concentrated by rotary evaporation. The residue was purified by silica gelcolumn chromatography to afford the product 8 (62 mg, 96%). Spectral data matches the cited literature.$^{[8,9]}$

$^1$H-NMR (CDCl$_3$, 400 MHz) δ: 7.28-7.24 (m, 2H), 7.22-7.15 (m, 3H), 5.68-5.62 (m, 1H), 5.60-5.54 (m, 1H), 3.39 (d, J = 8.0 Hz, 2H), 1.80 (d, J = 8.0 Hz, 2H), 1.25 (s, 12H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ: 141.2, 128.4, 128.2, 128.0, 125.7, 125.2, 83.2, 33.3, 24.7 ppm; IR (neat): 3022, 2980, 2928, 1328, 1145, 968, 739 cm$^{-1}$; HRMS (ESI-TOF) m/z calcd for C$_{16}$H$_{23}$BO$_2$Na (M + Na)$^+$: 281.1689, found 281.1693.

5-2. The reaction of 8 with 2a.

A stirring bar containing oven dried 25-ml Schlenk tube was charged with Cu(OTf)$_2$ (9.1 mg, 0.025 mmol, 10 mol%), PPh$_3$ (7.2 mg, 0.0275 mmol, 11 mol%), B$_2$Pin$_2$ (127 mg, 0.50 mmol, 2.0 equiv) and LiO$^-$Bu (40 mg, 0.50 mmol, 2.0 equiv). The tube was then evacuated and back-filled under a N$_2$ flow (this sequence was repeated three times). The intermediate 8 (65 mg, 0.25 mmol, 1.0 equiv), water (13.5 μL, 3.0 equiv), anhydrous DCE (1.0 ml) were added subsequently under N$_2$ condition. The reaction mixture was stirred for 1.5 h at r.t. and then 2a (53 mg, 0.50 mmol, 2.0 equiv) dissolved in anhydrous DCE (0.5 ml) were added, the tube was stirred at 70 ºC for 24h. After cooling to r.t, the reaction mixture diluted with EtOAc (10 ml) and H$_2$O (10 ml). Then it was extracted with EtOAc (10 ml × 3). The organic layer was combined and dried over Na$_2$SO$_4$, filtered and concentrated by rotary evaporation. The residue was purified by silica gelcolumn chromatography to afford the product 3aa (46 mg, 78%, 8:1 dr).
5-3. Deuterium labeling experiment

\[
\text{Ph} - \text{Ph} + \text{Ph} - \text{O} \quad \xrightarrow{\text{Cu(OTf)}_2 (10 \text{ mol\%), PPh}_3 (11 \text{ mol\%}), \text{LiO}^+\text{Bu (2.0 equiv), B}_2\text{Pin}_2 (2.0 equiv)} \quad \text{D}_2\text{O (3.0 equiv), DCE, 70 °C, N}_2 \quad \text{Ph} - \text{Ph} \quad \text{OH} - \text{Ph}
\]

\[3\text{aa-D}: 92\% \text{ yield,} \quad >20:1 \text{ dr; } d\% = 71\%
\]
6. Analytical data for compounds

(E)-1-(buta-1,3-dien-1-yl)-4-iodobenzene 64% yield, (1k): ¹H-NMR (CDCl₃, 400 MHz) δ: 7.63 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 6.78 (dd, J₁ = 16 Hz, J₂ = 12 Hz, 1H), 6.53-6.44 (m, 2H), 5.36 (d, J = 20 Hz, 1H), 5.21 (d, J = 12 Hz, 1H); ¹³C-NMR (CDCl₃, 100 MHz) δ: 137.6, 136.8, 136.6, 131.6, 130.4, 128.1, 118.4, 92.8 ppm; IR (neat): 3033, 3006, 2962, 1481, 1416, 1003, 811 cm⁻¹; HRMS (ESI-TOF) m/z calcd for C₁₄H₉Na (M + Na)⁺: 278.9647, found 278.9651.

2-benzyl-1-phenylbut-3-en-1-ol (3aa): The general procedure was followed using (E)-buta-1,3-dien-1-ylbenzene (1a, 33 mg, 0.25 mmol) and benzaldehyde (2a, 53 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1:10) afforded product 3aa as a colorless oil (56 mg, 93% yield, >20:1 dr); ¹H-NMR (CDCl₃, 400 MHz) δ: 7.33-7.21 (m, 7H), 7.16-7.10 (m, 3H), 5.60-5.51 (m, 1H), 4.95 (d, J = 8.0 Hz, 1H), 4.81 (d, J = 16 Hz, 1H), 4.70-4.67 (m, 1H), 2.93 (dd, J₁ = 16 Hz, J₂ = 4.0 Hz, 1H), 2.80-2.73 (m, 1H), 2.60-2.54 (m, 1H), 2.19-2.11 (m, 1H); ¹³C-NMR (CDCl₃, 100 MHz) δ: 142.3, 140.0, 137.5, 129.2, 128.1, 127.5, 125.8, 117.7, 76.3, 52.7, 36.1 ppm; IR (neat): 3417, 3081, 3029, 2924, 1494, 1452, 916 cm⁻¹; HRMS (ESI-TOF) m/z calcd for C₁₇H₁₈ONa (M + Na)⁺: 261.1255, found 261.1242.

2-(2-methylbenzyl)-1-phenylbut-3-en-1-ol (3ba): The general procedure was followed using (E)-1-(buta-1,3-dien-1-yl)-2-methylbenzene (1b, 36 mg, 0.25 mmol) and benzaldehyde (2a, 53 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1:10) afforded product 3ba as a colorless oil (56 mg, 88% yield, >20:1 dr); ¹H-NMR (CDCl₃, 400 MHz) δ: 7.35-7.27 (m, 5H), 7.06-7.02 (m, 4H), 5.66-5.57 (m, 1H), 4.93 (d, J = 8.0 Hz, 1H), 4.77-4.73 (m, 2H), 2.97-2.93 (m, 1H), 2.69-2.66 (m, 1H), 2.52-2.46 (m, 1H), 2.21 (brs, 1H), 2.15 (s, 3H); ¹³C-NMR (CDCl₃, 100 MHz) δ: 142.4, 138.3, 137.7, 136.2, 130.0, 129.9, 128.1, 127.5, 126.7, 125.8, 117.6, 76.7, 51.8, 33.0, 19.4 ppm; IR (neat): 3427, 3065, 3025, 2925, 1491, 1454, 746 cm⁻¹; HRMS (ESI-TOF) m/z calcd for C₁₈H₂₀ONa (M + Na)⁺: 275.1412, found 275.1413.

2-(3-methylbenzyl)-1-phenylbut-3-en-1-ol (3ca): The general procedure was followed using (E)-1-(buta-1,3-dien-1-yl)-3-methyl-benzene (1c, 36 mg, 0.25 mmol) and benzaldehyde (2a, 53 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1:10) afforded product 3ca as a colorless oil (50 mg, 78% yield, >20:1 dr); ¹H-NMR (CDCl₃, 400 MHz) δ: 7.35-7.25 (m, 5H), 7.14-7.11 (m, 1H), 6.97-6.95 (m, 1H), 6.92-6.90 (m, 2H), 5.60-5.51 (m, 1H), 4.96 (d, J = 8.0 Hz, 1H), 4.84 (d, J = 16 Hz, 1H), 4.73-4.63 (m, 1H), 2.90-2.86 (m, 1H), 2.80-2.73 (m, 1H), 2.57-2.51 (m, 1H), 2.29 (s, 3H), 2.14(brs, 1H); ¹³C-NMR (CDCl₃, 100 MHz) δ: 142.3, 139.9, 137.7, 137.6, 130.0, 128.1, 127.9, 127.5, 126.8, 126.5, 126.3, 117.6, 76.4, 52.6, 36.1, 21.4 ppm; IR (neat): 3415, 3062, 3028, 2920, 1490, 1452, 701 cm⁻¹; HRMS (ESI-TOF) m/z calcd for C₁₈H₂₀ONa (M + Na)⁺: 275.1412, found 275.1413.
2-(4-methylbenzyl)-1-phenylbut-3-en-1-ol (3da): The general procedure was followed using (E)-1-(buta-1,3-dien-1-yl)-4-methyl-benzene (1d, 36 mg, 0.25 mmol) and benzaldehyde (2a, 53 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product 3da as a colorless oil (32 mg, 51% yield, >20:1 dr): Rf = 0.5 (EtOAc : petroleum ether = 1 : 5); \( ^1H\)-NMR (CDCl₃, 400 MHz) \( \delta \): 7.36-7.25 (m, 5H), 7.05 (d, \( J = 8.0 \) Hz, 2H), 7.01 (d, \( J = 8.0 \) Hz, 1H), 6.60 (d, \( J = 12 \) Hz, 1H), 4.69 (d, \( J = 4.0 \) Hz, 1H), 2.90-2.85 (m, 1H), 2.79-2.72 (m, 1H), 2.57-2.51 (m, 1H), 2.29 (s, 3H), 2.15 (brs, 1H); \( ^13C\)-NMR (CDCl₃, 100 MHz) \( \delta \): 157.6, 142.3, 137.6, 136.8, 135.2, 129.1, 128.9, 128.1, 127.5, 126.8, 117.7, 76.3, 52.7, 35.7, 21.0 ppm; IR (neat): 3407, 3026, 2978, 2835, 1514; HRMS (ESI-TOF) m/z calcd for C₁₈H₂₀O⁻Na (M + Na)⁻: 275.1412, found 275.1402.

2-(4-methoxybenzyl)-1-phenylbut-3-en-1-ol (3ea): The general procedure was followed using (E)-1-(buta-1,3-dien-1-yl)-4-methoxybenzene (1e, 41 mg, 0.25 mmol) and benzaldehyde (2a, 53 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product 3ea as a colorless solid (52 mg, 78% yield, >20:1 dr): Rf = 0.4 (EtOAc : petroleum ether = 1 : 5); \( ^1H\)-NMR (CDCl₃, 400 MHz) \( \delta \): 7.35-7.25 (m, 5H), 7.02 (d, \( J = 8.0 \) Hz, 2H), 6.78 (d, \( J = 8.0 \) Hz, 2H), 5.59-5.50 (m, 1H), 4.96 (d, \( J = 12 \) Hz, 1H), 4.82 (d, \( J = 16 \) Hz, 1H), 4.67 (d, \( J = 4.0 \) Hz, 1H), 3.74 (s, 3H), 2.86 (dd, \( J = 12 \) Hz, \( J = 4.0 \) Hz, 1H), 2.73-2.69 (m, 1H), 2.55-2.50 (m, 1H), 2.21 (brs, 1H); \( ^13C\)-NMR (CDCl₃, 100 MHz) \( \delta \): 157.6, 142.3, 137.7, 132.0, 130.1, 128.1, 127.5, 126.7, 117.7, 113.4, 76.3, 55.1, 52.8, 35.3 ppm; IR (neat): 3383, 3031, 2919, 2835, 1512, 1451, 702 cm⁻¹; HRMS (ESI-TOF) m/z calcd for C₁₈H₂₀O⁻Na (M + Na)⁻: 291.1361, found 291.1359.

2-(4-(dimethylamino)benzyl)-1-phenylbut-3-en-1-ol (3fa): The general procedure was followed using (E)-4-(buta-1,3-dien-1-yl)-N,N-dimethylaniline (1f, 43 mg, 0.25 mmol) and benzaldehyde (2a, 53 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 5) afforded product 3fa as a yellow oil (48.5 mg, 69% yield, >20:1 dr): Rf = 0.3 (EtOAc : petroleum ether = 1 : 5); \( ^1H\)-NMR (CDCl₃, 400 MHz) \( \delta \): 7.35-7.24 (m, 5H), 7.00 (d, \( J = 8.0 \) Hz, 2H), 6.65 (d, \( J = 8.0 \) Hz, 2H), 5.60-5.51 (m, 1H), 4.97 (d, \( J = 8.0 \) Hz, 1H), 4.86 (d, \( J = 16 \) Hz, 1H), 4.67 (d, \( J = 4.0 \) Hz, 1H), 2.88 (s, 6H), 2.82-2.70 (m, 2H), 2.54-2.49 (m, 1H), 2.23 (brs, 1H); \( ^13C\)-NMR (CDCl₃, 100 MHz) \( \delta \): 148.9, 142.3, 137.9, 129.8, 128.0, 127.9, 127.4, 126.8, 117.5, 112.7, 76.2, 52.7, 40.8, 35.3 ppm; IR (neat): 3419, 3069, 3028, 2799, 1952, 1614, 702 cm⁻¹; HRMS (ESI-TOF) m/z calcd for C₁₈H₂₀O⁻Na (M + Na)⁻: 282.1858, found 282.1855.

2-(4-(dimethylamino)benzyl)-1-phenylbut-3-en-1-ol (3fa): The general procedure was followed using (E)-4-(buta-1,3-dien-1-yl)-N,N-dimethylaniline (1f, 43 mg, 0.25 mmol) and benzaldehyde (2a, 53 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 5) afforded product 3fa as a yellow oil (48.5 mg, 69% yield, >20:1 dr): Rf = 0.3 (EtOAc : petroleum ether = 1 : 5); \( ^1H\)-NMR (CDCl₃, 400 MHz) \( \delta \): 7.35-7.24 (m, 5H), 7.00 (d, \( J = 8.0 \) Hz, 2H), 6.65 (d, \( J = 8.0 \) Hz, 2H), 5.60-5.51 (m, 1H), 4.97 (d, \( J = 8.0 \) Hz, 1H), 4.86 (d, \( J = 16 \) Hz, 1H), 4.67 (d, \( J = 4.0 \) Hz, 1H), 2.88 (s, 6H), 2.82-2.70 (m, 2H), 2.54-2.49 (m, 1H), 2.23 (brs, 1H); \( ^13C\)-NMR (CDCl₃, 100 MHz) \( \delta \): 148.9, 142.3, 137.9, 129.8, 128.0, 127.9, 127.4, 126.8, 117.5, 112.7, 76.2, 52.7, 40.8, 35.3 ppm; IR (neat): 3419, 3069, 3028, 2799, 1952, 1614, 702 cm⁻¹; HRMS (ESI-TOF) m/z calcd for C₁₈H₂₀O⁻Na (M + Na)⁻: 282.1858, found 282.1855.
1-phenyl-2-(4-(trifluoromethyl)benzyl)but-3-en-1-ol (3ha): The general procedure was followed using (E)-1-(buta-1,3-dien-1-yl)-4-(trifluoromethyl)benzene (1h, 50 mg, 0.25 mmol) and benzaldehyde (2a, 53 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product 3ha as a colorless oil (59 mg, 77% yield, 16:1 dr): Rf = 0.5 (EtOAc : petroleum ether), 1H-NMR (CDCl3, 400 MHz) δ: 7.48 (d, J = 8.0 Hz, 2H), 7.36-7.26 (m, 5H), 7.20 (d, J = 8.0 Hz, 2H), 5.59-5.50 (m, 1H), 4.95 (d, J = 12 Hz, 1H), 4.77 (d, J = 16 Hz, 1H), 4.68 (d, J = 8.0 Hz, 1H), 3.03-3.00 (m, 1H), 2.74-2.72 (m, 1H), 2.65-2.62 (m, 1H), 2.23 (brs, 1H); 13C-NMR (CDCl3, 100 MHz) δ: 144.4, 142.2, 137.0, 129.6, 128.2, 127.7, 126.6, 124.9 (q, J = 4.8 Hz), 118.13, 76.4, 52.6, 35.9 ppm; HRMS (ESI-TOF) m/z calcd for C18H15F3O (M + Na)+: 305.1153, found 305.1152.

2-(4-chlorobenzyl)-1-phenylbut-3-en-1-ol (3ia): The general procedure was followed using (E)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene (1i, 41 mg, 0.25 mmol) and benzaldehyde (2a, 53 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 5): Rf = 0.5 (EtOAc : petroleum ether), 1H-NMR (CDCl3, 400 MHz) δ: 7.53-7.45 (m, 5H), 7.19 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 8.0 Hz, 2H), 5.57-5.48 (m, 1H), 4.95 (d, J = 12 Hz, 1H), 4.78 (d, J = 16 Hz, 1H), 4.67 (d, J = 4.0 Hz, 1H), 2.91 (dd, J = 12 Hz, J = 4.0 Hz, 1H), 2.72-2.64 (m, 1H), 2.57-2.51 (m, 1H), 2.14 (brs, 1H); 13C-NMR (CDCl3, 100 MHz) δ: 142.3, 138.6, 137.3, 131.5, 130.6, 128.2, 128.1, 127.6, 126.6, 118.0, 52.8, 35.5 ppm; IR (neat): 3412, 3068, 3032, 2927, 1640, 703 cm⁻¹; HRMS (ESI-TOF) m/z calcd for C18H14ClO (M + Na)+: 295.0866, found 295.0858.

2-(4-bromobenzyl)-1-phenylbut-3-en-1-ol (3ja): The general procedure was followed using (E)-1-bromo-4-(buta-1,3-dien-1-yl)benzene (1j, 52 mg, 0.25 mmol) and benzaldehyde (2a, 53 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 5): Rf = 0.5 (EtOAc : petroleum ether), 1H-NMR (CDCl3, 400 MHz) δ: 7.35-7.33 (m, 4H), 7.30-7.24 (m, 3H), 6.98-6.91 (m, 2H), 5.57-5.48 (m, 1H), 4.95 (d, J = 8.0 Hz, 1H), 4.78 (d, J = 16 Hz, 1H), 4.72-4.62 (m, 1H), 2.92-2.88 (m, 1H), 2.73-2.66 (m, 1H), 2.56-2.50 (m, 1H), 2.18-2.08 (m, 1H); 13C-NMR (CDCl3, 100 MHz) δ: 142.2, 139.1, 137.2, 131.1, 131.0, 128.2, 127.6, 126.6, 119.5, 118.0, 76.4, 52.7, 35.5 ppm; IR (neat): 3411, 3066, 3029, 2924, 1488, 1010, 704 cm⁻¹; HRMS (ESI-TOF) m/z calcd for C18H14BrO (M + Na)+: 314.1004, found 314.1004.
calcd for C_{17}H_{17}BrONa (M + Na)^+: 339.0360, found 339.0360.

2-(4-iodobenzyl)-1-phenylbut-3-en-1-ol (3ka): The general procedure was followed using (E)-1-(buta-1,3-dien-1-yl)-4-iodobenzene (1k, 64 mg, 0.25 mmol) and benzaldehyde (2a, 53 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product 3ka as a yellow liquid (72 mg, 78% yield, 18:1 dr): R_f = 0.5 (EtOAc : petroleum ether = 1 : 5); \^1H-NMR (CDCl_3, 400 MHz) δ: 7.54 (d, J = 8.0 Hz, 2H), 7.36-7.24 (m, 5H), 6.85 (d, J = 8.0 Hz, 2H), 5.57-5.48 (m, 1H), 4.96 (d, J = 12 Hz, 1H), 4.79 (d, J = 16 Hz, 1H), 4.70-4.63 (m, 1H), 2.91-2.87 (m, 1H), 2.73-2.66 (m, 1H), 2.52-2.44 (m, 1H), 2.14-2.06 (m, 1H); \^13C-NMR (CDCl_3, 100 MHz) δ: 142.2, 139.7, 137.2, 137.0, 131.4, 128.2, 127.6, 126.6, 118.0, 91.0, 76.3, 52.6, 35.6 ppm; IR (neat): 3433, 3067, 3029, 2925, 1725, 1485, 704 cm\(^{-1}\); HRMS (ESI-TOF) m/z calcd for C_{17}H_{16}IO (M -H)\(^+\): 363.0246, found 363.0248.

2-(naphthalen-2-ylmethyl)-1-phenylbut-3-en-1-ol (3la): The general procedure was followed using (E)-2-(buta-1,3-dien-1-yl)naphthalene (1l, 45 mg, 0.25 mmol) and benzaldehyde (2a, 53 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 5) afforded product 3la as a yellow solid (63 mg, 88% yield, >20:1 dr): R_f = 0.4 (EtOAc : petroleum ether = 1 : 5); \^1H-NMR (CDCl_3, 400 MHz) δ: 7.77-7.70 (m, 3H), 7.54 (s, 1H), 7.43-7.38 (m, 2H), 7.36-7.24 (m, 6H), 5.63-5.54 (m, 1H), 4.92 (d, J = 8.0 Hz, 1H), 4.80 (d, J = 16 Hz, 1H), 4.72 (d, J = 4.0 Hz, 1H), 3.08 (dd, J\(^1\) = 12 Hz, J\(^2\) = 4.0 Hz, 1H), 2.89-2.82 (m, 1H), 2.76-2.67 (m, 1H), 2.21 (brs, 1H); \^13C-NMR (CDCl_3, 100 MHz) δ: 142.3, 137.6, 137.5, 133.4, 131.9, 128.1, 127.9, 127.54, 127.50, 127.4, 126.7, 125.7, 125.1, 117.8, 76.4, 52.6, 36.4 ppm; IR (neat): 3383, 3007, 2916, 2852, 1452, 1007, 733 cm\(^{-1}\); HRMS (ESI-TOF) m/z calcd for C_{21}H_{20}ONa (M + Na)^+: 311.1412, found 311.1405.

2-(furan-2-ylmethyl)-1-phenylbut-3-en-1-ol (3ma): The general procedure was followed using (E)-2-(buta-1,3-dien-1-yl)furan (1m, 30 mg, 0.25 mmol) and benzaldehyde (2a, 53 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1:10) afforded product 3ma as a colorless oil (35 mg, 61% yield, 14:1 dr): R_f = 0.5 (EtOAc : petroleum ether = 1 : 5); \^1H-NMR (CDCl_3, 400 MHz) δ: 7.35-7.25 (m, 6H), 6.29-6.21 (m, 1H), 6.03-5.95 (m, 1H), 5.65-5.56 (m, 1H), 4.92 (d, J = 8.0 Hz, 1H), 4.80 (d, J = 16 Hz, 1H), 4.72 (d, J = 4.0 Hz, 1H), 3.08 (dd, J\(^1\) = 12 Hz, J\(^2\) = 4.0 Hz, 1H), 2.89-2.82 (m, 1H), 2.76-2.67 (m, 1H), 2.21 (brs, 1H); \^13C-NMR (CDCl_3, 100 MHz) δ: 154.0, 142.0, 140.9, 137.5, 128.1, 127.6, 126.7, 117.5, 110.1, 106.3, 76.0, 49.9, 28.6 ppm; IR (neat): 3432, 3114, 3030, 2924, 1452, 1009, 733 cm\(^{-1}\); HRMS (ESI-TOF) m/z calcd for C_{15}H_{16}O_{2}Na (M + Na)^+: 251.1048, found 251.1045.

1-phenyl-2-(thiophen-3-ylmethyl)but-3-en-1-ol (3na): The general procedure was followed using (E)-3-(buta-1,3-dien-1-yl)thiophene (1n, 34 mg, 0.25 mmol) and benzaldehyde (2a, 53 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product 3na as a yellow liquid (49 mg, 80% yield, 13:1 dr): R_f = 0.5 (EtOAc : petroleum ether = 1 : 5); \^1H-NMR (CDCl_3, 400 MHz) δ: 7.28-7.16 (m, 5H), 7.13 (m, 1H), 6.83-6.81 (m, 2H), 5.55-5.46
(m, 1H), 4.93 (d, J = 8 Hz, 1H), 4.83 (d, J = 16 Hz, 1H), 4.59-4.58 (m, 1H), 2.82 (dd, J₁= 12 Hz, J₂= 4.0 Hz 1H), 2.73-2.66 (m, 1H), 2.63-2.57 (m, 1H), 2.08 (brs, 1H); ¹³C-NMR (CDCl₃, 100 MHz) δ: 142.2, 140.2, 137.8, 128.7, 128.1, 127.5, 126.7, 124.9, 121.2, 117.7, 76.2, 51.8, 30.7 ppm; IR (neat): 3429, 3079, 3030, 2923, 1451, 917, 763 cm⁻¹; HRMS (ESI-TOF) m/z cale for C₁₇H₂₂OSNa (M + Na)⁺: 267.0820, found 267.0806.

1,5-diphenyl-2-vinylpent-1-ol (3oa): The general procedure was followed using (E)-hexa-3,5-dien-1-ylbenzene (1o, 40 mg, 0.25 mmol) and benzaldehyde (2a, 53 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 5) afforded product 3oa as a colorless oil (29 mg, 43% yield, 6:1 dr): Rf = 0.5 (EtOAc : petroleum ether = 1 : 4); ¹H-NMR (CDCl₃, 400 MHz) δ: 7.27-7.18 (m, 7H), 7.10-6.98 (m, 3H), 5.46-5.37 (m, 1H), 4.99-4.89 (m, 2H), 4.53-4.51 (m, 1H), 2.56-2.21 (m, 3H), 2.06-1.95 (m, 1H), 1.57-1.47 (m, 1H), 1.18-1.09 (m, 9H), 0.79 (t, J = 6.0 Hz, 3H); ¹³C-NMR (CDCl₃, 100 MHz) δ: 142.5, 138.5, 128.0, 127.4, 126.7, 125.6, 117.5, 76.9, 51.3, 35.9, 29.3, 29.2 ppm; HRMS (ESI-TOF) m/z cale for C₁₉H₂₃ONa (M + Na)⁺: 289.1568, found 289.1571.

1-phenyl-2-vinyloctan-1-ol (3pa): The general procedure was followed using (E)-nona-1,3-diene (1p, 31 mg, 0.25 mmol) and benzaldehyde (2a, 53 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 5) afforded product 3pa as a yellow liquid (24 mg, 41% yield, 7:1 dr): Rf = 0.6 (EtOAc : petroleum ether = 1 : 5); ¹H-NMR (CDCl₃, 400 MHz) δ: 7.27-7.18 (m, 5H), 5.47-5.38 (m, 1H), 5.01-4.91 (m, 2H), 4.58-4.51 (m, 1H), 2.34-2.32 (m, 1H), 2.01-1.95 (m, 1H), 1.57-1.47 (m, 1H), 1.18-1.09 (m, 9H), 0.79 (t, J = 6.0 Hz, 3H); ¹³C-NMR (CDCl₃, 100 MHz) δ: 142.5, 138.5, 128.0, 127.3, 126.7, 117.3, 76.9, 51.4, 31.8, 29.6, 29.3, 27.2, 22.6, 14.1 ppm; IR (neat): 3411, 3067, 3029, 2855, 1455, 1024, 702 cm⁻¹; HRMS (ESI-TOF) m/z cale for C₁₉H₂₄ONa (M + Na)⁺: 255.1725, found 255.1719.

2-(cyclohexylmethyl)-1-phenylbut-3-en-1-ol (3qa): The general procedure was followed using (E)-buta-1,3-dien-1-ylcyclohexane (1q, 34 mg, 0.25 mmol) and benzaldehyde (2a, 53 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 5) afforded product 3qa as a colorless oil (28 mg, 45% yield, 7:1 dr): Rf = 0.6 (EtOAc : petroleum ether = 1 : 5); ¹H-NMR (CDCl₃, 400 MHz) δ: 7.34-7.25 (m, 5H), 5.54-5.45 (m, 1H), 5.09-5.00 (m, 2H), 4.61-4.58 (m, 1H), 2.60-2.54 (m, 1H), 2.07-2.06 (m, 1H), 1.74-1.55 (m, 5H), 1.32-1.11 (m, 6H), 0.95-0.67 (m, 2H); ¹³C-NMR (CDCl₃, 100 MHz) δ: 142.4, 138.7, 127.9, 127.3, 126.7, 117.2, 77.1, 48.3, 37.3, 34.63, 34.58, 32.1, 26.6, 26.4, 26.1 ppm; IR (neat): 3431, 3067, 3029, 2855, 1455, 1024, 702 cm⁻¹; HRMS (ESI-TOF) m/z cale for C₁₉H₂₄ONa (M + Na)⁺: 267.1725, found 267.1719.

A containing stirring bar oven dried 25-ml Schlenk tube was charged with Cu(OTf)₂ (9.1mg, 0.025 mmol, 10 mol%), PPH₃ (7.2mg, 0.0275 mmol, 11 mol%), B₃Pin₃ (127 mg, 0.50 mmol, 2.0 equiv) and LiO'Bu (40mg, 0.50 mmol, 2.0 equiv). The tube was then evacuated and back-filled under a N₂ flow (this sequence was repeated
Diene 1r (37 mg, 0.25 mmol, 1.0 equiv), water (13.5 μL, 3.0 equiv), anhydrous DCE (1.0 ml) were added subsequently under N₂ condition. The reaction mixture was stirred for 1.5 h at r.t and then 2a (53 mg, 0.50 mmol, 2.0 equiv) dissolved in anhydrous DCE (0.5 ml) were added, the tube was stirred at 70 °C for 48 h. After cooling to r.t, the reaction mixture diluted with EtOAc (10 ml) and H₂O (10 ml). Then it was extracted with EtOAc (10 ml × 3). The organic layer was combined and dried over Na₂SO₄, filtered and concentrated by rotary evaporation. The residue was purified by silica gel column chromatography to afford the product 3ra as a yellow liquid (31 mg, 49% yield, >20:1 dr): Rf = 0.6 (EtOAc : petroleum ether = 1 : 5); ¹H-NMR (CDCl₃, 400 MHz) δ: 7.23-7.11 (m, 5H), 5.81-5.74 (m, 1H), 5.22 (d, J = 12 Hz, 1H), 4.92 (d, J = 20 Hz, 1H), 4.38 (d, J = 8.0 Hz, 1H), 2.48 (t, J = 6.0 Hz, 1H), 2.19-2.13 (m, 2H), 1.76-1.69 (m, 4H), 1.26-1.24 (m, 1H), 1.18 (s, 3H), 1.16-1.13 (m, 1H), 0.72 (s, 3H); ¹³C-NMR (CDCl₃, 100 MHz) δ: 145.3, 141.5, 128.4, 127.4, 127.3, 115.0, 78.1, 48.8, 46.9, 40.1, 38.9, 28.1, 26.4, 25.7, 24.5, 23.7 ppm; IR (neat): 3458, 3078, 3028, 2917, 1409, 1042, 729 cm⁻¹; HRMS (ESI-TOF) m/z calcd for C₁₈H₂₄ONa (M + Na)⁺: 279.1725, found 279.1723.

2-benzyl-1-(o-tolyl)but-3-en-1-ol (3ab): The general procedure was followed using (E)-buta-1,3-dien-1-ylbenzene (1a, 33 mg, 0.25 mmol) and 2-methylbenzaldehyde (2b, 60 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product 3ab as a yellow oil (57 mg, 91% yield, >20:1 dr): Rf = 0.5 (EtOAc : petroleum ether = 1 : 5); ¹H-NMR (CDCl₃, 400 MHz) δ: 7.48 (d, J = 8.0 Hz, 1H), 7.23-7.20 (m, 3H), 7.18-7.07 (m, 5H), 5.69-5.60 (m, 1H), 4.96 (d, J = 4.0 Hz, 1H), 4.89 (d, J = 12 Hz, 1H), 4.75 (d, J = 16 Hz, 1H), 3.09 (t, J = 12 Hz, 1H), 2.75-2.63 (m, 2H), 2.31 (s, 3H), 1.98 (brs, 1H); ¹³C-NMR (CDCl₃, 100 MHz) δ: 141.0, 140.4, 138.1, 134.7, 130.4, 129.3, 128.0, 127.2, 126.4, 126.0, 125.7, 117.1, 73.1, 51.8, 35.4, 19.4 ppm; IR (neat): 3386, 3065, 3026, 2925, 1602, 1492, 700 cm⁻¹; HRMS (ESI-TOF) m/z calcd for C₁₈H₂₀ONa (M + Na)⁺: 275.1412, found 275.1406.

2-benzyl-1-(m-tolyl)but-3-en-1-ol (3ac): The general procedure was followed using (E)-buta-1,3-dien-1-ylbenzene (1a, 33 mg, 0.25 mmol) and 3-methylbenzaldehyde (2c, 60 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product 3ac as a colorless oil (59 mg, 93% yield, >20:1 dr): Rf = 0.5 (EtOAc : petroleum ether = 1 : 5); ¹H-NMR (CDCl₃, 400 MHz) δ: 7.25-7.20 (m, 3H), 7.15-7.14 (m, 1H), 7.12-7.07 (m, 5H), 5.69-5.60 (m, 1H), 4.96 (d, J = 4.0 Hz, 1H), 4.89 (d, J = 12 Hz, 1H), 4.75 (d, J = 16 Hz, 1H), 3.09 (d, J = 12 Hz, 1H), 2.75-2.63 (m, 2H), 2.31 (s, 3H), 1.98 (brs, 1H); ¹³C-NMR (CDCl₃, 100 MHz) δ: 142.3, 140.1, 137.7, 129.3, 128.0, 127.2, 126.4, 126.0, 125.7, 117.6, 76.4, 52.6, 36.1, 21.5 ppm; IR (neat): 3415, 3063, 3027, 2925, 1602, 1492, 700 cm⁻¹; HRMS (ESI-TOF) m/z calcd for C₁₈H₂₀ONa (M + Na)⁺: 275.1412, found 275.1406.

2-benzyl-1-(p-tolyl)but-3-en-1-ol (3ad): The general procedure was followed using (E)-buta-1,3-dien-1-ylbenzene (1a, 33 mg, 0.25 mmol) and 4-methyl benzaldehyde (2d, 60 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product 3ad as a colorless oil (60 mg, 94% yield, >20:1 dr): Rf = 0.5 (EtOAc : petroleum ether = 1 : 5).
Methyl 4-(2-benzyl-1-hydroxybut-3-en-1-yl) benzoate (3ae): The general procedure was followed using (E)-buta-1,3-dien-1-ylbenzene (1a, 33 mg, 0.25 mmol) and methyl 4-formylbenzaldehyde (2e, 82 mg, 0.50 mmol).

Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 5) afforded product 3ae as a colorless solid (68 mg, 91% yield, >20:1 dr): Rf = 0.3 (EtOAc : petroleum ether = 1 : 5); 1H-NMR (CDCl3, 400 MHz) δ: 7.99 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.25-7.21 (m, 2H), 7.17-7.13 (m, 1H), 7.09 (d, J = 8.0 Hz, 2H), 5.60-5.51 (m, 1H), 4.96 (d, J = 12 Hz, 1H), 4.83-4.75 (m, 2H), 3.89 (s, 3H), 2.89 (d, J = 12 Hz, 1H), 2.81-2.68 (m, 1H), 2.62-2.56 (m, 1H), 2.47 (brs, 1H); 13C-NMR (CDCl3, 100 MHz) δ: 167.0, 147.7, 139.7, 137.2, 129.3, 129.2, 129.1, 128.1, 126.7, 125.8, 118.0, 75.9, 52.7, 52.0, 35.9 ppm; IR (neat): 3503, 3068, 3029, 2854, 1707, 1288, 862 cm⁻¹; HRMS (ESI-TOF) m/z calcd for C19H19O2Na (M + Na)⁺: 319.1310, found 319.1305.

2-benzyl-1-(4-(trifluoromethyl)phenyl)but-3-en-1-ol (3af): The general procedure was followed using (E)-buta-1,3-dien-1-ylbenzene (1a, 33 mg, 0.25 mmol) and methyl 4-trifluoromethylbenzaldehyde (2f, 87 mg, 0.50 mmol).

Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product 3af as a yellow solid (73 mg, 95% yield, >20:1 dr): Rf = 0.5 (EtOAc : petroleum ether = 1 : 5); 1H-NMR (CDCl3, 400 MHz) δ: 7.59 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.26-7.23 (m, 2H), 7.18-7.15 (m, 1H), 7.11-7.09 (m, 2H), 5.60-5.51 (m, 1H), 4.99 (d, J = 12 Hz, 1H), 4.85 (d, J = 16 Hz, 1H), 4.77-4.75 (m, 1H), 2.89-2.85 (m, 1H), 2.80-2.74 (m, 1H), 2.63-2.57 (m, 1H), 2.24-2.23 (m, 1H); 13C-NMR (CDCl3, 100 MHz) δ: 146.3, 139.6, 137.0, 129.5, 129.2, 128.2, 127.0, 126.0, 125.0 (q, J = 4.0 Hz), 118.3, 75.7, 52.6, 35.9 ppm; 19F-NMR (CDCl3, 376 MHz) δ: -62.36 ppm; IR (neat): 3417, 3082, 3029, 2926, 1715, 1328, 841 cm⁻¹; HRMS (ESI-TOF) m/z calcd for C18H18F3O (M -H): 305.1153, found 305.1152.

2-benzyl-1-(4-methoxyphenyl)but-3-en-1-ol (3ag): The general procedure was followed using (E)-buta-1,3-dien-1-yl benzene (1a, 33 mg, 0.25 mmol) and methyl 4-methoxybenzaldehyde (2g, 68 mg, 0.50 mmol).

Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product 3ag as a colorless oil (60 mg, 89% yield, >20:1 dr): Rf = 0.4 (EtOAc : petroleum ether = 1 : 5); 1H-NMR (CDCl3, 400 MHz) δ: 7.26-7.21 (m, 4H), 7.17-7.11 (m, 3H), 6.86 (d, J = 8.0 Hz, 2H), 5.59-5.50 (m, 1H), 4.95 (d, J = 12 Hz, 1H), 4.81 (d, J = 20 Hz, 1H), 4.63 (d, J = 8.0 Hz, 1H), 3.79 (s, 3H), 2.93 (d, J = 16 Hz, 1H), 2.75-2.74 (m, 1H), 2.59-2.54 (m, 1H), 2.12 (brs, 1H); 13C-NMR (CDCl3, 100 MHz) δ: 158.9, 140.1, 137.6, 134.5, 129.3, 128.0, 127.9, 125.8, 117.6, 113.4, 76.0, 55.2, 52.7, 36.4 ppm; IR (neat): 3429, 3066, 3028, 2930, 1610, 1248, 717, 1288, 862 cm⁻¹; HRMS (ESI-TOF) m/z calcd for C19H18O2Na (M + Na)⁺: 319.1310, found 319.1305.
4-(2-benzyl-1-hydroxybut-3-en-1-yl)-2-methoxyphenyl acetate (3ah): The general procedure was followed using (E)-buta-1,3-dien-1-yl benzene (1a, 33 mg, 0.25 mmol) and methyl 4-formyl-2-methoxyphenyl acetate (2h, 97 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 6) afforded product 3ah as a yellow oil (70mg, 86% yield, >20:1 dr). \( \delta \) 7.26-7.22 (m, 2H), 7.17-7.11 (m, 3H), 6.99-6.94 (m, 2H), 6.86 (d, \( J = 8.0 \) Hz, 2H), 5.63-5.54 (m, 1H), 4.97 (d, \( J = 12 \) Hz, 1H), 4.83 (d, \( J = 16 \) Hz, 1H), 4.66 (d, \( J = 4.0 \) Hz, 1H), 3.80 (s, 3H), 2.93 (d, \( J = 12 \) Hz, 1H), 2.81-2.68 (m, 1H), 2.64-2.58 (m, 1H), 2.30-2.27 (m, 4H); IR (neat): 3405, 3076, 3027, 2921, 1614, 1349, 912 cm\(^{-1}\); HRMS (ESI-TOF) \( m/z \) calcd for C\(_{18}\)H\(_{20}\)O\(_2\)Na (M + Na\(^+\)): 291.1361, found 291.1358.

2-benzyl-1-(4-dimethylamino)phenyl-but-3-en-1-ol (3ai): The general procedure was followed using (E)-buta-1,3-dien-1-ylbenzene (1a, 33 mg, 0.25 mmol) and methyl 4-(dimethylamino)benzaldehyde (2i, 75 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 6) afforded product 3ai as a yellow oil (57mg, 81% yield, >20:1 dr): \( \delta \) 7.18-7.13 (m, 5H), 6.70 (d, \( J = 8.0 \) Hz, 2H), 5.60-5.51 (m, 1H), 4.94 (d, \( J = 8 \) Hz, 1H), 4.81 (d, \( J = 16 \) Hz, 1H), 4.59 (d, \( J = 4.0 \) Hz, 1H), 2.97-2.93 (m, 7H), 2.83-2.70 (m, 1H), 2.59-2.54 (m, 1H), 2.02 (brs, 1H); \(^{13}\)C-NMR (CDCl\(_3\), 100 MHz) \( \delta \): 169.1, 150.7, 141.4, 139.9, 137.4, 129.2, 128.1, 125.8, 122.2, 118.9, 117.7, 110.8, 76.0, 55.8, 52.5, 36.1, 20.6 ppm; IR (neat): 3462, 3076, 3027, 2926, 1764, 1456, 912 cm\(^{-1}\); HRMS (ESI-TOF) \( m/z \) calcd for C\(_{19}\)H\(_{22}\)O\(_2\)Na (M + Na\(^+\)): 349.1416, found 349.1404.

2-benzyl-1-(4-chlorophenyl)but-3-en-1-ol (3aj): The general procedure was followed using (E)-buta-1,3-dien-1-ylbenzene (1a, 33 mg, 0.25 mmol) and 4-chlorobenzaldehyde (2j, 70 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product 3aj as a yellow oil (57mg, 81% yield, >20:1 dr). \( \delta \) 7.32-7.30 (m, 2H), 7.26-7.23 (m, 4H), 7.18-7.09 (m, 3H), 7.07-7.04 (m, 2H), 7.02-6.99 (m, 2H), 6.89 (d, \( J = 8.0 \) Hz, 2H), 5.64-5.56 (m, 1H), 4.98 (d, \( J = 12 \) Hz, 1H), 4.83 (d, \( J = 20 \) Hz, 1H), 4.68-4.66 (m, 1H), 2.88 (dd, \( J_{1} = 12 \) Hz, \( J_{2} = 4.0 \) Hz, 1H), 2.74-2.71 (m, 1H), 2.60-2.55 (m, 1H), 2.14-2.13 (m, 1H); \(^{13}\)C-NMR (CDCl\(_3\), 100 MHz) \( \delta \): 140.8, 139.7, 137.2, 133.2, 129.2, 128.2, 128.12, 128.09, 125.9, 118.1, 75.7, 52.6, 36.1 ppm; IR (neat): 3431, 3081, 3028, 2925, 1600, 1491, 701 cm\(^{-1}\); HRMS (ESI-TOF) \( m/z \) calcd for C\(_{19}\)H\(_{17}\)ClNaO (M + Na\(^+\)): 295.0866, found 295.0870.

2-benzyl-1-(4-bromophenyl)but-3-en-1-ol(3ak): The general procedure was followed using (E)-buta-1,3-dien-1-ylbenzene (1a, 33 mg, 0.25 mmol) and 4-bromobenzaldehyde (2k, 93 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded
product 3ak as a colorless oil (69 mg, 87% yield, >20:1 dr): Rf = 0.4 (EtOAc: petroleum ether = 1: 5); 1H-NMR (CDCl3, 400 MHz) δ: 7.45 (d, J = 8.0 Hz, 2H), 7.26-7.22 (m, 2H), 7.17 (m, 3H), 7.10 (d, J = 8.0 Hz, 2H), 5.57-5.48 (m, 1H), 4.97 (d, J = 8.0 Hz, 1H), 4.82 (d, J = 16 Hz, 1H), 4.65 (d, J = 4.0 Hz, 1H), 2.87 (d, J = 16 Hz, 1H), 2.73-2.72 (m, 1H), 2.60-2.54 (m, 1H), 2.19 (brs, 1H); 13C-NMR (CDCl3, 100 MHz) δ: 141.3, 139.7, 137.1, 131.2, 129.2, 128.4, 128.1, 125.9, 121.3, 118.1, 75.7, 52.5, 36.1 ppm; IR (neat): 3413, 3080, 2977, 1640, 1490, 825 cm−1; HRMS (ESI-TOF) m/z calcd for C17H17BrONa (M + Na)+: 339.0360, found 339.0356.

2-benzyl-1-(3,4-dichlorophenyl)but-3-en-1-ol (3ai): The general procedure was followed using (E)-buta-1,3-dien-1-ylbenzene (1a, 33 mg, 0.25 mmol) and 3,4-dichlorobenzaldehyde (2i, 88 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc: petroleum ether = 1: 10) afforded product 3ai as a colorless oil (70 mg, 91% yield, >20:1 dr): Rf = 0.4 (EtOAc: petroleum ether = 1: 5); 1H-NMR (CDCl3, 400 MHz) δ: 7.32-7.30 (m, 2H), 7.18-7.15 (m, 2H), 7.10-7.07 (m, 1H), 7.05-7.01 (m, 3H), 5.50-5.41 (m, 1H), 4.92 (d, J = 12 Hz, 1H), 4.76 (d, J = 16 Hz, 1H), 4.60-4.50 (m, 1H), 2.79-2.76 (m, 1H), 2.64-2.63 (m, 1H), 2.54-2.48 (m, 1H), 2.17 (brs, 1H); 13C-NMR (CDCl3, 100 MHz) δ: 142.6, 139.4, 136.9, 132.2, 131.3, 130.0, 129.2, 128.7, 128.2, 126.1, 126.0, 118.4, 75.1, 52.5, 36.0 ppm; IR (neat): 3430, 3065, 3028, 2924, 1712, 1469, 884 cm−1; HRMS (ESI-TOF) m/z calcd for C17H15Cl2O (M-H)-: 305.0500, found 305.0502.

2-benzyl-1-(4-iodophenyl)-but-3-en-1-ol (3am): The general procedure was followed using (E)-buta-1,3-dien-1-ylbenzene (1a, 33 mg, 0.25 mmol) and 4-iodobenzaldehyde (2m, 116 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc: petroleum ether = 1: 10) afforded product 3am as a colorless oil (86 mg, 94% yield, >20:1 dr): Rf = 0.5 (EtOAc: petroleum ether = 1: 5); 1H-NMR (CDCl3, 400 MHz) δ: 7.65 (d, J = 8.0 Hz, 2H), 7.26-7.22 (m, 2H), 7.18-7.14 (m, 1H), 7.11-7.03 (m, 4H), 5.57-5.48 (m, 1H), 4.98 (d, J = 12 Hz, 1H), 4.83 (d, J = 20 Hz, 1H), 4.64-4.62 (m, 1H), 2.89-2.84 (m, 1H), 2.75-2.70 (m, 1H), 2.59-2.54 (m, 1H), 2.16-2.15 (m, 1H); 13C-NMR (CDCl3, 100 MHz) δ: 141.9, 139.7, 137.1, 129.2, 128.7, 128.1, 125.9, 118.1, 93.0, 75.8, 52.5, 36.1 ppm; IR (neat): 3402, 3079, 3027, 2977, 1640, 1490, 821 cm−1; HRMS (ESI-TOF) m/z calcd for C17H15I2O (M-H)-: 387.0222, found 387.0222.

1-(benzofuran-2-yl)-2-benzylbut-3-en-1-ol (3an): The general procedure was followed using (E)-buta-1,3-dien-1-ylbenzene (1a, 33 mg, 0.25 mmol) and benzofuran-2-carbaldehyde (2n, 73 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc: petroleum ether = 1: 8) afforded product 3an as a colorless solid (47 mg, 68% yield, >20:1 dr): Rf = 0.4 (EtOAc: petroleum ether = 1: 5); 1H-NMR (CDCl3, 400 MHz) δ: 7.54 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.26-7.16 (m, 7H), 6.62 (s, 1H), 5.75-5.66 (m, 1H), 5.07-4.98 (m, 2H), 4.81-4.78 (m, 1H), 3.01-2.93 (m, 2H), 2.72-2.66 (m, 1H), 2.34 (d, J = 8.0 Hz, 1H); 13C-NMR (CDCl3, 100 MHz) δ: 157.6, 154.7, 139.5, 136.9, 129.3, 128.2, 127.9, 126.0, 124.1, 122.8, 121.0, 118.5, 111.2, 104.1, 70.2, 51.0, 36.6 ppm; IR (neat): 3350, 3029, 2925, 2856, 1420, 1253, 919 cm−1; HRMS (ESI-TOF) m/z calcd for C19H16O2Na (M + Na)+: 301.1204, found 301.1196.
2-benzyl-1-(2,2-difluorobenzo[d][1,3]dioxol-5-yl)but-3-en-1-ol (3ao): The general procedure was followed using (E)-buta-1,3-dien-1-ylbenzene (1a, 33 mg, 0.25 mmol) and 2,2-difluorobenzo[d][1,3]dioxole-5-carbaldehyde (2o, 93 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product 3ao as a yellow oil (64mg, 81% yield, >20:1 dr): R_f = 0.4 (EtOAc : petroleum ether = 1 : 5); ^1H-NMR (CDCl_3, 400 MHz) δ: 7.27-7.23 (m, 2H), 7.17-7.14 (m, 3H), 7.01-6.97 (m, 2H), 5.58-5.49 (m, 1H), 4.99 (d, J = 12 Hz, 1H), 4.83 (d, J = 16 Hz, 1H), 4.68-4.67 (m, 1H), 2.92-2.87 (m, 1H), 2.76-2.69 (m, 1H), 2.63-2.57 (m, 1H), 2.15 (m, 1H); ^13C-NMR (CDCl_3, 100 MHz) δ: 143.7, 142.9, 139.5, 138.7, 137.0, 134.1, 131.6, 129.2, 126.0, 121.9, 118.3, 108.8, 108.0, 75.8, 52.7, 36.2 ppm; ^19F-NMR (CDCl_3, 376 MHz) δ: -49.73, -49.71, -49.74, -50.00 ppm; IR (neat): 3414, 3083, 3029, 2925, 1642, 1448, 816 cm^{-1}; HRMS (ESI-TOF) m/z calcd for C_{18}H_{13}F_{2}O (M - H)^+: 317.0989, found 317.0972.

2-benzyl-1-cyclohexylbut-3-en-1-ol (3ap): The general procedure was followed using (E)-buta-1,3-dien-1-ylbenzene (1a, 33 mg, 0.25 mmol) and cyclohexanecarbaldehyde (2p, 56 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 25) afforded product 3ap as a colorless oil (48mg, 79% yield, 8:1 dr): R_f = 0.7 (EtOAc : petroleum ether = 1 : 5); ^1H-NMR (CDCl_3, 400 MHz) δ: 7.27-7.23 (m, 2H), 7.17-7.14 (m, 3H), 5.67-5.58 (m, 1H), 4.98 (d, J = 12 Hz, 1H), 4.84 (d, J = 16 Hz, 1H), 3.33-3.14 (m, 1H), 3.05 (d, J = 12 Hz, 1H), 2.72-2.51 (m, 2H), 1.77-1.53 (m, 7H), 1.25-1.02 (m, 5H); ^13C-NMR (CDCl_3, 100 MHz) δ: 140.5, 139.0, 129.4, 128.0, 125.7, 116.4, 78.3, 48.7, 40.3, 36.0, 30.2, 26.5, 26.4, 26.0 ppm; IR (neat): 3412, 3067, 3028, 2851, 1639, 1449, 741 cm^{-1}; HRMS (ESI-TOF) m/z calcd for C_{17}H_{23}O (M + Na)^+: 267.1725, found 267.1724.

4-benzyl-1-phenylhex-5-en-3-ol (3aq): The general procedure was followed using (E)-buta-1,3-dien-1-ylbenzene (1a, 33 mg, 0.25 mmol) and 3-phenylpropanal (2q, 67 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product 3aq as a colorless solid (53mg, 80% yield, 7:1 dr): R_f = 0.4 (EtOAc : petroleum ether = 1 : 5); ^1H-NMR (CDCl_3, 400 MHz) δ: 7.22-7.01 (m, 10H), 5.59-5.50 (m, 1H), 4.98-4.83 (m, 2H), 2.65-2.59 (m, 1H), 2.48-2.41 (m, 1H), 2.35-2.26 (m, 1H), 2.15-2.10 (m, 1H), 1.87-1.55 (m, 3H); ^13C-NMR (CDCl_3, 100 MHz) δ: 142.1, 140.0, 137.9, 129.1, 128.3, 128.3, 128.1, 125.8, 125.8, 117.7, 73.0, 52.3, 36.9, 35.7, 32.3 ppm; IR (neat): 3385, 3318, 3083, 2937, 1452, 1085, 699 cm^{-1}; HRMS (ESI-TOF) m/z calcd for C_{19}H_{26}O (M + Na)^+: 289.1568, found 289.1563.

3-benzynon-1-en-4-ol (3ar): The general procedure was followed using (E)-buta-1,3-dien-1-ylbenzene (1a, 33 mg, 0.25 mmol) and hexanal (2r, 50 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 3ar as a colorless oil (46mg, 79% yield, 9:1 dr): R_f = 0.7 (EtOAc : petroleum ether = 1 : 5); ^1H-NMR (CDCl_3, 400 MHz) δ: 7.27-7.24 (m, 2H), 7.18-7.14 (m, 3H), 5.69-5.60 (m, 1H), 5.04 (d, J = 12 Hz, 1H), 4.92 (d, J = 16 Hz, 1H), 3.61-3.46 (m, 1H), 2.91 (dd, J_1 = 12 Hz, J_2 = 4.0 Hz, 1H), 2.65-2.59 (m, 1H), 2.48-2.41 (m, 1H), 2.35-2.26 (m, 1H), 2.15-2.10 (m, 1H), 1.87-1.55 (m, 3H);
1.62-1.45 (m, 3H), 1.31-1.23 (m, 6H), 0.89 (t, \(J = 6\) Hz, 3H); \(^{13}\text{C-NMR}\) (CDCl\(_3\), 100 MHz) \(\delta\): 140.2, 138.3, 129.2, 128.1, 125.8, 117.4, 73.7, 52.2, 36.7, 33.8, 31.8, 25.6, 22.6, 14.0 ppm; \(\text{IR}\) (neat): 3348, 3083, 2921, 2857, 1494, 918, 698 cm\(^{-1}\); \(\text{HRMS (ESI-TOF)}\) \(m/z\) calcd for C\(_{16}\)H\(_{24}\)ONa (M + Na\(^{+}\)): 255.1725, found 255.1724.

3-benzyl-8-chlorooct-1-en-4-ol (3as): The general procedure was followed using (\(E\))-buta-1,3-dien-1-ylbenzene (1a, 33 mg, 0.25 mmol) and 4-chlorobutanal (2s, 60 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product 3as as a colorless oil (50mg, 78% yield, 8:1 dr); \(R_f = 0.4\) (EtOAc : petroleum ether = 1 : 5); \(^1\text{H-NMR}\) (CDCl\(_3\), 400 MHz) \(\delta\): 7.28-7.24 (m, 2H), 7.19-7.14 (m, 3H), 5.68-5.59 (m, 1H), 5.05 (d, \(J = 8.0\) Hz, 1H), 4.94 (d, \(J = 16\) Hz, 1H), 3.55-3.52 (m, 3H), 2.93-2.88 (m, 1H), 2.66-2.60 (m, 1H), 2.49-2.45 (m, 1H), 1.83-1.74 (m, 2H), 1.64-1.58 (m, 2H), 1.47-1.46 (m, 1H), 1.40-1.26 (m, 2H); \(^{13}\text{C-NMR\)} (CDCl\(_3\), 100 MHz)\(\delta\): 140.0, 138.0, 129.2, 128.1, 125.9, 117.6, 73.4, 52.2, 44.9, 36.8, 33.0, 32.5, 23.3 ppm; \(\text{IR}\) (neat): 3391, 3079, 3027, 2928, 1495, 916, 702 cm\(^{-1}\); \(\text{HRMS (ESI-TOF)}\) \(m/z\) calcd for C\(_{15}\)H\(_{23}\)ClONa (M + Na\(^{+}\)): 275.1179, found 275.1184.
7. Further transformations for the product

7-1 Procedure for synthesis of 4 \(^{11}\)

A containing stirring bar oven dried 10 ml Schlenk tube was charged with 3-chlorobenzoperoxoic acid (76mg, 0.375 mmol). The tube was then evacuated and back-filled under a N\(_2\) flow (this sequence was repeated three times). A solution of 3aa (60 mg, 0.25 mmol) in dry DCM (1.3 ml) was added by syringe. The reaction mixture was stirred overnight at room temp under N\(_2\) and was diluted with DCM (3 ml). After having been washed with saturated solution of K\(_2\)CO\(_3\) (2 × 10 ml), the organic layer was separated and dried with Na\(_2\)SO\(_4\), and solvent was removed under reduced pressure. The product was purified by silica gel column chromatography (EtOAc : petroleum ether = 1 : 8) to afford the product 4 (53 mg, 83% yield, 3:1 dr): R\(_f\) = 0.3 (EtOAc : petroleum ether = 1 : 5); \(^1\)H-NMR (CDCl\(_3\), 400 MHz) \(\delta\): 7.40-7.02 (m, 10H), 5.03-4.64 (m, 1H), 2.99-2.10 (m, 6H), 1.79-1.74 (m, 1H); \(^13\)C-NMR (CDCl\(_3\), 100 MHz) \(\delta\): 142.7, 142.1, 139.7, 139.1, 129.6, 128.9, 128.4, 128.30, 127.9, 127.4, 126.3, 126.14, 126.08, 74.8, 74.0, 53.1, 52.9, 50.7, 49.9, 47.6, 47.4, 33.7, 32.4 ppm; IR (neat): 3442, 3060, 3025, 2925, 1602, 1451, 887 cm\(^{-1}\); HRMS (ESI-TOF) m/z calcd for C\(_{17}\)H\(_{18}\)O\(_2\)Na (M + Na\(^+\)): 277.1204, found 277.1204.

7-2 Procedure for synthesis of 5 \(^{12}\)

A containing stirring bar oven dried 10 ml Schlenk tube was charged with Pd(OAc)\(_2\) (0.0185 mmol, 4.1 mg). The tube was then evacuated and back-filled under a N\(_2\) flow (this sequence was repeated three times). Et\(_3\)N (1.85 mmol, 187 mg), iodobenzene (0.37 mmol, 75.5 mg) and a solution of 3aa (0.185 mmol, 44.1 mg) in dry MeCN (1.8 ml) was added by syringe. The reaction mixture was stirred at 85\(^\circ\)C for 18 h under N\(_2\) and then cooled to room temperature. The mixture was concentrated in vacuo and residue was purified by silica gel column chromatography (EtOAc : petroleum ether = 1 : 10) to afford the product 5 (41 mg, 70% yield): R\(_f\) = 0.4 (EtOAc : petroleum ether = 1 : 5); \(^1\)H-NMR (CDCl\(_3\), 400 MHz) \(\delta\): 7.36-7.33 (m, 4H), 7.28-7.12 (m, 11H), 6.16 (d, \(J\) = 16 Hz, 1H), 5.98-5.92 (m, 1H), 4.83-4.74 (m, 1H), 2.98-2.88 (m, 2H), 2.71-2.66 (m, 1H), 2.15-2.14 (m, 1H); \(^13\)C-NMR (CDCl\(_3\), 100 MHz) \(\delta\): 142.2, 139.9, 137.3, 132.5, 129.4, 129.3, 128.4, 128.1, 127.5, 127.1, 126.7, 126.1, 125.8, 76.6, 51.9, 36.7 ppm; IR (neat): 3391, 3060, 3025, 2914, 1451, 1005, 743, 696 cm\(^{-1}\); HRMS (ESI-TOF) m/z calcd for C\(_{23}\)H\(_{22}\)ONa (M + Na\(^+\)): 337.1568, found 337.1562.
7-3 Procedure for synthesis of \(6^{13}\)

![Image](image.png)

In an oven dried 10 ml Schlenk tube, BH\(_3\)SMe\(_2\) (0.3 ml, 2.0 M, 0.6 mmol, 3.0 equiv) was added to a solution of 3aa (0.20 mmol, 48 mg, 1.0 equiv) in dry THF (2.0 ml) at 0°C. The reaction mixture was stirred at room temperature under N\(_2\) for 3 h, then an aqueous solution of 10% NaOH (0.36 ml, 4.5 equiv) and 30% H\(_2\)O\(_2\) (0.12 ml, 6.0 equiv) were added. After stirring for 3 h, the mixture was extracted with EtOAc (3 × 10 ml). The organic layer was separated and dried with Na\(_2\)SO\(_4\), and solvent was removed under reduced pressure. The product was purified by silica gel column chromatography (EtOAc : petroleum ether = 1 : 2) to afford the product 6 (32 mg, 60% yield): \(R_f = 0.5\) (EtOAc : petroleum ether = 1 : 1); \(^1\)H-NMR (CDCl\(_3\), 400 MHz) \(\delta\): 7.37-7.34 (m, 4H), 7.29-7.21 (m, 3H), 7.16-7.13 (m, 1H), 7.07-7.06 (m, 2H), 4.89-4.81 (m, 1H), 3.67-3.50 (m, 4H), 2.73-2.70 (m, 1H), 2.47-2.41 (m, 1H), 2.31-2.18 (m, 1H), 1.67-1.62 (m, 1H), 1.49-1.45 (m, 1H); \(^13\)C-NMR (CDCl\(_3\), 100 MHz) \(\delta\): 142.7, 140.6, 129.1, 128.3, 128.2, 127.2, 126.5, 125.8, 75.7, 60.8, 45.1, 34.8, 32.2 ppm; IR (neat): 3350, 3061, 3027, 2930, 1493, 1451, 702 cm\(^{-1}\); HRMS (ESI-TOF) \(m/z\) calcd for C\(_{17}\)H\(_{20}\)O\(_2\)Na (M + Na\(^+\)): 279.1361, found 279.1357.

7-4 Procedure for synthesis of \(7^{14}\)

![Image](image.png)

A containing stirring bar oven dried 10 ml Schlenk tube was charged with CuI (0.02 mmol, 3.8 mg). The tube was then evacuated and back-filled under a N\(_2\) flow (this sequence was repeated three times). Pentamethyldiethylenetriamine (0.3 mmol, 52 mg), a solution of 3aa (0.20 mmol, 48 mg) in dry MeCN (0.8 ml) and ethylbromodifluoroacetate (0.30 mmol, 61 mg) was added subsequently. The reaction mixture was heated to 80°C. After stirring for 12 h, the reaction was cooled to room temperature. The reaction mixture was diluted with EtOAc and filtered with a pad of Celite. The filtrate was concentrated, and the residue was purified with silica gel chromatography (EtOAc : petroleum ether = 1 : 8) to give the product 7 (31 mg, 43% yield): \(R_f = 0.5\) (EtOAc : petroleum ether = 1 : 5); \(^1\)H-NMR (CDCl\(_3\), 400 MHz) \(\delta\): 7.35-7.33 (m, 2H), 7.29-7.22 (m, 5H), 7.18-7.14 (m, 1H), 7.08-7.06 (m, 2H), 6.09-6.03 (m, 1H), 5.29 (dd, \(J_f = 28\) Hz, \(J_f = 12\) Hz, 1H), 4.72 (d, 1H, 1H), 4.15 (q, 1H, 1H), 3.03-2.99 (m, 1H), 2.86-2.73 (m, 1H), 2.66-2.61 (m, 1H), 2.08 (s, 1H), 1.23 (t, 1H, 1H); \(^13\)C-NMR (CDCl\(_3\), 100 MHz) \(\delta\): 163.7 (t, 1H, 35 Hz), 141.8, 139.0, 138.5 (t, 1H, 9.0 Hz), 129.3, 128.3, 128.2, 127.9, 126.5, 126.1, 123.5 (t, 1H, 25.5 Hz), 111.8 (t, 1H, 247 Hz), 76.0, 62.7, 51.4, 36.0, 13.8 ppm; \(^19\)F-NMR (CDCl\(_3\), 376 MHz) \(\delta\): -103.35, -104.02, -104.23, -104.91 ppm; IR (neat): 3441, 3063, 3030, 2924, 1764, 1670, 702 cm\(^{-1}\); HRMS (ESI-TOF) \(m/z\) calcd for C\(_{21}\)H\(_{22}\)F\(_2\)O\(_3\)Na (M + Na\(^+\)): 383.1435, found 383.1427.
8. References


525
3ad

![Chemical Structure](image)

![NMR Spectrum](image)

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)
S95
$1k$