Supporting Information

Introduction of Prenyl Fragment into Chalcones through α-Regioselective 1,2-Addition in THF

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1 General Methods

α,β-unsaturated carbonyl compounds were prepared by condensation reactions of respective aldehydes and ketones. Solvents were treated prior to use according to the standard methods. Other reagents were used as purchased without further purification.

¹H NMR and ¹³C NMR spectra were recorded at 400 MHz and 100 MHz in CDCl₃ with chemical shift (δ) given in ppm relative to TMS as internal standard. Multiplicities are indicated, s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet); coupling constant (J) are in Hertz (Hz). High resolution mass spectra (HRMS) were recorded using a TOF instrument using electrospray ionization (ESI).

2 General Procedure for the Synthesis of 2a-r

Prenyl bromide (2.0 mmol) was added into a suspension of activated zinc powder (2.5 mmol) in dry THF (10 ml); the reaction mixture was stirred for 1 h at room temperature. Filtered the solution through a Schlenk filter and kept under N₂ for the following reaction. A solution of chalcones 1 (1.0 mmol) in dry THF (5 ml) was added the solution of prenylzinc bromide prepared above. The mixture was refluxed for 10 h. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate, 40/1, v/v) to afford the α-adducts 2a-r.

3 General Procedure for the Synthesis of 2s and 2t

Prenyl bromide (2.0 mmol) was added into a suspension of activated zinc powder (2.5 mmol) in dry THF (10 ml); the reaction mixture was stirred for 1 h at room temperature. Filtered the solution through a Schlenk filter and kept under N₂ for the following reaction. A solution of α,β-unsaturated carbonyl compounds 1 (1.0 mmol) in dry THF (5 ml) was added the solution of prenylzinc bromide prepared above. The solution was stirred for 1 h at room temperature. Then DMI (1.5 ml) was added into the reaction mixture, followed by removal of initial reaction solvent (THF). The mixture was heated to 120 °C for 14 h. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate, 40/1, v/v) to afford the α-adducts 2s and 2t.
4 General Procedure for the Synthesis of 3a, 3h, 3j, 3l, and 3w

Crotyl bromide (2.0 mmol) was added into a suspension of activated zinc powder (2.5 mmol) in dry THF (10 ml); the reaction mixture was stirred for 1 h at room temperature. Filtered the solution through a Schlenk filter and kept under N\textsubscript{2} for the following reaction. A solution of chalcones 1 (1.0 mmol) in dry THF (5 ml) was added the solution of crotylzinc bromide prepared above. The mixture was refluxed for 10 h. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate, 40/1, v/v) to afford the \(\alpha\)-adducts 3a, 3h, 3j, 3l, and 3w.

5 Characterization of 2a-r

Characterization of 2a:

![Structure of 2a]

Colorless oil; \(^1\)H NMR (CDCl\textsubscript{3}, 400 MHz) \(\delta\): 7.50 (d, \(J = 8.0\) Hz, 2H), 7.41 (d, \(J = 8.4\) Hz, 2H), 7.36 (t, \(J = 8.0\) Hz, 2H), 7.27-7.22 (m, 3H), 6.58 (d, \(J = 16.0\) Hz, 1H), 6.50 (d, \(J = 16.0\) Hz, 1H), 5.07 (t, \(J = 7.6\) Hz, 1H), 2.80-2.70 (m, 2H), 2.30 (s, 1H), 1.71 (s, 3H), 1.66 (s, 3H). \(^{13}\)C NMR (CDCl\textsubscript{3}, 100 MHz) \(\delta\): 145.5, 137.7, 136.4, 135.9, 131.6, 128.3, 128.1, 126.9, 125.4, 121.1, 117.9, 76.4, 41.2, 26.1, 18.2. HRMS (ESI): m/z calcd for C\textsubscript{20}H\textsubscript{21}OBrNa [M + Na]\(^+\): 379.0673; Found: 379.0673.

Characterization of 2b:

![Structure of 2b]

Yellow oil; \(^1\)H NMR (CDCl\textsubscript{3}, 400 MHz) \(\delta\): 7.52 (d, \(J = 8.0\) Hz, 2H), 7.42-7.18 (m, 8H), 6.64 (d, \(J = 16.0\) Hz, 1H), 6.53 (d, \(J = 16.0\) Hz, 1H), 5.09 (t, \(J = 7.8\) Hz, 1H), 2.83-2.67 (m, 2H), 2.28 (s, 1H), 1.71 (s, 3H), 1.66 (s, 3H). \(^{13}\)C NMR (CDCl\textsubscript{3}, 100 MHz) \(\delta\): 145.8, 137.6, 136.9,
135.6, 128.6, 128.3, 128.1, 127.5, 126.9, 126.6, 125.3, 118.1, 76.4, 41.3, 26.1, 18.2. HRMS (ESI): m/z calcd for C₂₀H₂₂ONa [M + Na]⁺: 301.1568; Found: 301.1568.

Characterization of 2c:

Yellow oil; ¹H NMR (CDCl₃, 400 MHz) δ: 7.51 (d, J = 8.0 Hz, 2H), 7.37 (t, J = 7.8 Hz, 2H), 7.33-7.23 (m, 5H), 6.60 (d, J = 16.0 Hz, 1H), 6.49 (d, J = 16.0 Hz, 1H), 5.07 (t, J = 7.0 Hz, 1H), 2.83-2.65 (m, 2H), 2.28 (s, 1H), 1.71 (s, 3H), 1.66 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ: 145.5, 137.8, 136.3, 135.5, 133.0, 128.7, 128.3, 127.8, 126.9, 126.8, 125.5, 117.9, 76.4, 41.2, 26.1, 18.2. HRMS (ESI): m/z calcd for C₂₀H₂₁ClONa [M + Na]⁺: 335.1179; Found: 335.1179.

Characterization of 2d:

Colorless oil; ¹H NMR (CDCl₃, 400 MHz) δ: 7.58 (d, J = 7.6 Hz, 2H), 7.38 (t, J = 7.6 Hz, 2H), 7.33-7.23 (m, 3H), 7.08 (t, J = 8.0 Hz, 1H), 6.67 (d, J = 16.4 Hz, 1H), 6.52 (d, J = 16.4 Hz, 1H), 5.23 (t, J = 7.2 Hz, 1H), 2.84-2.67 (m, 2H), 2.35 (s, 1H), 1.74 (s, 3H), 1.67 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ: 145.2, 143.5, 137.5, 134.8, 134.5, 128.3, 128.0, 127.0, 125.7, 122.4, 118.2, 76.6, 41.0, 26.2, 18.2. HRMS (ESI): m/z calcd for C₂₀H₂₀Cl₂ONa [M + Na]⁺: 369.0789; Found: 369.0806.

Characterization of 2e:
Pale yellow oil; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\): 7.52 (d, \(J = 8.4\) Hz, 2H), 7.35 (t, \(J = 8.0\) Hz, 2H), 7.31-7.21 (m, 3H), 7.11 (d, \(J = 8.0\) Hz, 2H), 6.60 (d, \(J = 16.0\) Hz, 1H), 6.47 (d, \(J = 16.0\) Hz, 1H), 5.09 (t, \(J = 8.0\) Hz, 1H), 2.90-2.58 (m, 2H), 2.32 (s, 3H), 2.26 (s, 1H), 1.71 (s, 3H), 1.66 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\): 145.9, 137.4, 137.3, 134.6, 134.1, 129.3, 128.2, 128.0, 126.8, 126.5, 125.6, 118.2, 76.7, 41.3, 26.1, 21.2, 18.3. HRMS (ESI): m/z calcd for C\(_{21}\)H\(_{24}\)ONa [M + Na]\(^+\): 315.1725; Found: 315.1727.

Characterization of 2f:

Colorless oil; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\): 7.52 (d, \(J = 7.6\) Hz, 2H), 7.40-7.28 (m, 4H), 7.28-7.20 (m, 1H), 6.82 (d, \(J = 8.0\) Hz, 2H), 6.57 (d, \(J = 16.0\) Hz, 1H), 6.39 (d, \(J = 16.0\) Hz, 1H), 5.09 (t, \(J = 8.0\) Hz, 1H), 3.80 (s, 3H), 2.87-2.63 (m, 2H), 2.26 (s, 1H), 1.71 (s, 3H), 1.66 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\): 159.1, 146.0, 137.3, 133.5, 129.7, 128.2, 127.7, 127.6, 126.8, 125.6, 118.2, 114.0, 76.5, 55.3, 41.4, 26.1, 18.3. HRMS (ESI): m/z calcd for C\(_{21}\)H\(_{24}\)O\(_2\)Na [M + Na]\(^+\): 331.1674; Found: 331.1665.

Characterization of 2g:

Pale yellow oil; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\): 7.45 (d, \(J = 8.8\) Hz, 2H), 7.38 (d, \(J = 7.2\) Hz, 2H), 7.35-7.20 (m, 5H), 6.62 (d, \(J = 16.0\) Hz, 1H), 6.48 (d, \(J = 16.0\) Hz, 1H), 5.06 (t, \(J = 8.0\) Hz, 1H), 3.80 (s, 3H), 2.87-2.63 (m, 2H), 2.26 (s, 1H), 1.71 (s, 3H), 1.66 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\): 159.1, 146.0, 137.3, 133.5, 129.7, 128.2, 127.7, 127.6, 126.8, 125.6, 118.2, 114.0, 76.5, 55.3, 41.4, 26.1, 18.3. HRMS (ESI): m/z calcd for C\(_{21}\)H\(_{24}\)O\(_2\)Na [M + Na]\(^+\): 331.1674; Found: 331.1665.
Hz, 1H), 2.80-2.61 (m, 2H), 2.28 (s, 1H), 1.71 (s, 3H), 1.66 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 144.3, 138.0, 136.7, 135.0, 132.7, 128.6, 128.5, 128.3, 127.7, 127.1, 126.6, 117.7, 76.1, 41.2, 26.2, 18.3. HRMS (ESI): m/z calcd for C$_{20}$H$_{21}$ClONa [M + Na]$^+$: 335.1179; Found: 335.1168.

Characterization of 2h:

Pale yellow oil; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.40 (d, $J = 8.0$ Hz, 2H), 7.33-7.25 (m, 4H), 7.23 (t, $J = 7.6$ Hz, 2H), 7.16 (t, $J = 7.6$ Hz, 1H), 6.54 (d, $J = 16.0$ Hz, 1H), 6.39 (d, $J = 16.0$ Hz, 1H), 4.98 (t, $J = 7.2$ Hz, 1H), 2.65-2.63 (m, 2H), 2.21 (s, 1H), 1.64 (s, 3H), 1.58 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 144.8, 138.1, 136.6, 135.0, 131.3, 128.6, 128.5, 127.7, 127.5, 126.6, 120.8, 117.6, 76.2, 41.2, 26.2, 18.3. HRMS (ESI): m/z calcd for C$_{20}$H$_{21}$BrONa [M + Na]$^+$: 379.0673; Found: 379.0659.

Characterization of 2i:

Pale yellow oil; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.41 (d, $J = 8.0$ Hz, 2H), 7.38 (d, $J = 8.0$ Hz, 2H), 7.30 (t, $J = 7.6$ Hz, 2H), 7.24-7.16 (m, 3H), 6.64 (d, $J = 16.0$ Hz, 1H), 6.52 (d, $J = 16.0$ Hz, 1H), 5.11 (t, $J = 7.2$ Hz, 1H), 2.80-2.69 (m, 2H), 2.35 (s, 3H), 2.25 (s, 1H), 1.72 (s, 3H), 1.67 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 142.8, 137.3, 137.0, 136.5, 135.8, 129.0, 128.5, 127.9, 127.4, 126.6, 125.5, 118.3, 76.4. HRMS (ESI): m/z calcd for C$_{21}$H$_{24}$ONa [M + Na]$^+$: 315.1725; Found: 315.1724.

Characterization of 2j:
Yellow oil; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.48 (d, $J = 8.0$ Hz, 2H), 7.40 (d, $J = 8.0$ Hz, 2H), 7.17-7.15 (m, 3H), 6.85 (d, $J = 16.0$ Hz, 1H), 6.35 (d, $J = 16.0$ Hz), 5.09 (t, $J = 7.2$ Hz, 1H), 2.76-2.66 (m, 2H), 2.33 (s, 3H), 2.29 (s, 1H), 1.73 (s, 3H), 1.66 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 145.0, 138.8, 137.8, 136.4, 136.0, 135.7, 131.3, 130.3, 127.6, 127.6, 126.5, 126.1, 125.7, 120.8, 117.8, 76.4, 41.3, 26.2, 19.9, 18.3. HRMS (ESI): m/z calcd for C$_{21}$H$_{23}$BrONa [M + Na]$^+$: 393.0830; Found: 393.0824.

Characterization of 2k:

Yellow oil; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.48 (d, $J = 8.0$ Hz, 2H), 7.40 (d, $J = 8.0$ Hz, 2H), 7.23-7.17 (m, 3H), 7.04 (d, $J = 6.4$ Hz, 1H), 6.59 (d, $J = 16.0$ Hz, 1H), 6.46 (d, $J = 16.0$ Hz, 1H), 5.07 (t, $J = 7.2$ Hz, 1H), 2.76-2.67 (m, 2H), 2.34 (s, 3H), 2.27 (s, 1H), 1.72 (s, 3H), 1.66 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 145.0, 138.3, 138.0, 136.8, 135.0, 131.4, 128.8, 128.6, 127.6, 127.4, 123.9, 121.0, 117.9, 76.4, 41.3, 26.3, 21.5, 18.4. HRMS (ESI): m/z calcd for C$_{21}$H$_{23}$BrONa [M + Na]$^+$: 393.0830; Found: 393.0830.

Characterization of 2l:

Yellow oil; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.48 (d, $J = 8.0$ Hz, 2H), 7.40 (d, $J = 8.0$ Hz, 2H), 7.25-7.23 (m, 1H), 6.98 (d, $J = 8.0$ Hz, 1H), 6.92 (s, 1H), 6.80 (d, $J = 8.0$ Hz, 1H), 6.60 (d, $J =
16.0 Hz, 1H), 6.47 (d, J = 16.0 Hz, 1H), 5.07 (t, J = 7.2 Hz, 1H), 3.81 (s, 3H), 2.73-2.71 (m, 2H), 2.34 (s, 1H), 1.72 (s, 3H), 1.66 (s, 3H). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz) δ: 160.0, 144.9, 138.3, 138.1, 135.5, 131.4, 129.7, 128.6, 127.6, 121.0, 119.4, 117.8, 113.5, 112.0, 76.3, 55.4, 41.3, 26.2, 18.4. HRMS (ESI): m/z calcd for C\textsubscript{21}H\textsubscript{23}BrO\textsubscript{2}Na [M + Na\textsuperscript{+}]: 409.0779; Found: 409.0780.

Characterization of 2m:

\[
\begin{array}{c}
\text{Br} \\
\text{H} \\
\text{O} \\
\end{array}
\]

Yellow oil; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) δ: 7.48 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.23-7.17 (m, 3H), 7.04 (d, J = 6.4 Hz, 1H), 6.59 (d, J = 16.0 Hz, 1H), 6.46 (d, J = 16.0 Hz, 1H), 5.07 (t, J = 7.2 Hz, 1H), 2.76-2.67 (m, 2H), 2.34 (s, 3H), 2.27 (s, 1H), 1.72 (s, 3H), 1.66 (s, 3H). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz) δ: 145.0, 138.3, 138.0, 136.8, 135.0, 131.4, 128.8, 128.6, 127.6, 127.4, 123.9, 121.0, 117.9, 76.4, 41.3, 26.3, 21.5, 18.4. HRMS (ESI): m/z calcd for C\textsubscript{21}H\textsubscript{23}BrONa [M + Na\textsuperscript{+}]: 393.0830; Found: 393.0826.

Characterization of 2n:

\[
\begin{array}{c}
\text{F} \\
\text{H} \\
\end{array}
\]

Yellow oil; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) δ: 7.45-7.38 (m, 3H), 7.20-7.14 (m, 3H), 7.06 (d, J = 7.6 Hz, 1H), 7.01 (dd, J = 8.8 Hz, J = 10.8 Hz, 1H), 6.80 (d, J = 16.0 Hz, 1H), 6.60 (d, J = 16.0 Hz, 1H), 5.09 (t, J = 6.8 Hz, 1H), 2.81-2.68 (m, 2H), 2.34 (s, 3H), 2.27 (s, 1H), 1.71 (s, 3H), 1.66 (s, 3H). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz) δ: 160.5 (J = 247.9 Hz), 142.8, 138.5 (J = 4.4 Hz), 137.5, 136.6, 129.1, 128.7 (J = 8.0 Hz), 127.8 (J = 3.7 Hz), 125.6, 125.0, 124.9, 124.1 (J = 3.6 Hz), 120.5 (J = 2.9 Hz), 118.3, 115.9, 115.7, 76.6, 41.3, 26.2, 21.4, 18.4. HRMS (ESI): m/z calcd for C\textsubscript{21}H\textsubscript{23}FONa [M + Na\textsuperscript{+}]: 333.1631; Found: 333.1631.
Characterization of 2o:

Colorless oil; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.80 (d, $J = 7.6$ Hz, 1H), 7.58 (d, $J = 7.6$ Hz, 1H), 7.36-7.24 (m, 5H), 7.12 (t, $J = 7.2$ Hz, 1H), 6.87 (d, $J = 16.0$ Hz, 1H), 6.52 (d, $J = 16.0$ Hz, 1H), 5.07 (t, $J = 7.6$ Hz, 1H), 3.12-2.92 (m, 2H), 2.65 (s, 1H), 1.70 (s, 3H), 1.67 (s, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 144.1, 137.3, 135.6, 134.9, 134.8, 133.2, 128.8, 128.7, 128.5, 127.8, 127.4, 120.8, 118.0, 76.8, 38.8, 26.1, 18.2. HRMS (ESI): m/z calcd for C$_{20}$H$_{20}$BrClONa [M + Na]$^+$: 413.0284; Found: 413.0292.

Characterization of 2p:

Colorless oil; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.40 (d, $J = 8.0$ Hz, 2H), 7.21-7.14 (m, 5H), 7.03 (t, $J = 3.2$ Hz, 1H), 6.59 (d, $J = 16.0$ Hz, 1H), 6.49 (d, $J = 16.0$ Hz, 1H), 5.11 (t, $J = 7.6$ Hz, 1H), 2.78-2.68 (m, 2H), 2.34 (s, 3H), 2.32 (s, 3H), 2.23 (s, 1H), 1.71 (s, 3H), 1.66 (s, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 143.0, 138.2, 137.4, 137.1, 136.6, 135.8, 129.1, 128.6, 128.4, 128.1, 127.4, 125.6, 123.9, 118.5, 76.5, 41.4, 26.3, 21.5, 21.2, 18.4. HRMS (ESI): m/z calcd for C$_{22}$H$_{26}$ONa [M + Na]$^+$: 329.1881; Found: 329.1876.

Characterization of 2q:

Yellow oil; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.50 (d, $J = 8.0$ Hz, 2H), 7.36 (t, $J = 8.0$ Hz, 2H), 7.27-7.23 (m, 1H), 7.14-7.13 (m, 1H), 6.94-6.93(m, 2H), 6.76 (d, $J = 16.0$ Hz, 1H), 6.36 (d, J
= 16.0 Hz, 1H), 5.07 (t, J = 7.2 Hz, 1H), 2.78-2.67 (m, 2H), 2.26 (s, 1H), 1.71 (s, 3H), 1.66 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz) δ: 145.7, 142.4, 137.8, 135.4, 128.4, 127.5, 127.1, 125.9, 125.7, 124.2, 121.8, 118.1, 76.4, 41.4, 26.2, 18.4. HRMS (ESI): m/z calcd for C$_{18}$H$_{20}$OSNa [M + Na]$^+$: 307.1133; Found: 307.1134.

Characterization of 2r:

Yellow oil; $^1$H NMR (CDCl$_3$, 400 MHz) δ: 7.52 (s, 1H), 7.48 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.8 Hz, 1H), 7.26 (d, J = 7.2 Hz, 1H), 7.16 (t, J = 8.0 Hz, 1H), 6.56 (d, J = 16.0 Hz, 1H), 6.46 (d, J = 16.0 Hz, 1H), 5.03 (t, J = 7.2 Hz, 1H), 2.73-2.71 (m, 2H), 2.28 (s, 1H), 1.72 (s, 3H), 1.66 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz) δ: 144.4, 138.9, 138.5, 136.5, 131.4, 130.5, 130.1, 129.3, 127.4, 127.0, 125.3, 122.8, 121.0, 117.3, 76.1, 41.1, 26.2, 18.3. HRMS (ESI): m/z calcd for C$_{20}$H$_{20}$Br$_2$ONa [M + Na]$^+$: 456.9779; Found: 456.9780.

Characterization of 2s:

Yellow oil; $^1$H NMR (CDCl$_3$, 400 MHz) δ: 7.39 (d, J = 8.0 Hz, 2H), 7.32 (t, J = 8.0 Hz, 2H), 7.22 (t, J = 8.0 Hz, 1H), 6.59 (d, J = 16.0 Hz, 1H), 6.30 (d, J = 16.0 Hz, 1H), 5.19 (t, J = 7.8 Hz, 1H), 2.46-2.25 (m, 2H), 1.78 (s, 1H), 1.74 (s, 3H), 1.38 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz) δ: 137.1, 136.7, 136.2, 128.6, 127.3, 127.1, 126.4, 118.8, 73.3, 41.4, 27.9, 26.1, 18.1. HRMS (ESI): m/z calcd for C$_{15}$H$_{20}$ONa [M + Na]$^+$: 239.1412; Found: 239.1421.

Characterization of 2t:
Yellow oil; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.32 (d, $J = 8.0$ Hz, 2H), 6.86 (d, $J = 8.0$ Hz, 2H), 6.54 (d, $J = 16.0$ Hz, 1H), 6.12 (dd, $J = 6.4$ Hz, $J = 16.0$ Hz, 1H), 5.20 (t, $J = 7.2$ Hz, 1H), 4.28 (s, 1H), 3.81 (s, 3H), 2.39-2.31 (m, 2H), 1.75 (s, 3H), 1.66 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 159.0, 135.3, 129.6, 129.5, 129.3, 127.4, 119.2, 113.7, 72.5, 55.1, 36.2, 25.7, 17.8. HRMS (ESI): m/z calcd for C$_{15}$H$_{20}$O$_2$Na [M + Na]$^+$: 255.1361; Found: 255.1353.

Characterization of 2u:

Pale yellow oil; $^1$H NMR (400MHz, CDCl$_3$) $\delta$: 7.39-7.37 (m, 2H), 7.33-7.30 (m, 2H), 7.25-7.22 (m, 1H), 6.58 (d, $J = 16.0$ Hz, 1H), 6.25 (d, $J = 16.0$ Hz, 1H), 5.20 (s, 2H), 2.43-2.27 (m, 4H), 1.86 (s, 1H), 1.73 (s, 6H), 1.64 (s, 6H). $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 137.3, 135.7, 135.6, 128.6, 127.9, 127.2, 126.4, 118.8, 75.6, 39.6, 26.1, 18.1. HRMS (ESI): m/z calcd for C$_{19}$H$_{26}$ONa [M + Na]$^+$: 293.1881; Found: 293.1889.

Characterization of 2v:

Pale yellow oil; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.36 (s, 1H), 7.24-7.19 (m, 3H), 6.54 (d, $J = 16.0$ Hz, 1H), 6.26 (d, $J = 16.0$ Hz, 1H), 5.18 (t, $J = 7.2$ Hz, 1H), 2.43-2.37 (m, 2H), 2.32-2.26 (m, 2H), 1.87 (s, 1H), 1.74 (s, 6H), 1.64 (s, 6H). $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 139.2, 137.3, 136.0, 134.5, 129.8, 127.1, 126.7, 126.2, 124.7, 118.5, 75.5, 39.5, 26.1, 18.1. HRMS (ESI): m/z calcd for C$_{19}$H$_{25}$ClONa [M + Na]$^+$: 327.1492; Found: 327.1490.
6 Characterization of 3a, 3h, 3j, 3l, and 3w:

Characterization of 3a:

![Structure of 3a]

Yellow oil; $^1$H NMR (CDCl$_3$, 400 MHz) δ: 7.51 (t, $J = 7.6$ Hz, 2H), 7.41 (d, $J = 7.2$ Hz, 2H), 7.37 (t, $J = 8.0$ Hz, 2H), 7.30-7.22 (m, 3H), 6.61 (d, $J = 10.4$ Hz, 0.28H, isomer 1), 6.57 (d, $J = 10.8$ Hz, 0.72H, isomer 2), 6.54 (d, $J = 14.0$ Hz, 0.73H, isomer 2), 6.50 (d, $J = 16.0$ Hz, 0.27H, isomer 1), 5.75-5.62 (m, 1H), 5.38-5.26 (m, 1H), 2.83-2.69 (m, 2H), 2.36 (s, 0.48H, isomer 1), 2.26 (s, 0.52H, isomer 2), 1.66 (t, $J = 6.0$ Hz, 3H). $^{13}$C NMR (CDCl$_3$, 100 Hz): 145.4, 145.4, 136.4, 136.3, 136.0, 136.0, 132.0, 131.8, 131.8, 129.6, 128.5, 128.5, 128.2, 127.2, 127.2, 127.1, 127.1, 125.6, 125.6, 125.1, 124.2, 121.4, 121.4, 76.5, 75.7, 46.0, 40.0, 18.3, 13.4. HRMS (ESI): m/z calcd for C$_{19}$H$_{19}$OBrNa [M + Na]$^+$: 365.0517; Found: 365.0517.

Characterization of 3h:

![Structure of 3h]

Yellow oil; $^1$H NMR (CDCl$_3$, 400 MHz) δ: 7.48 (d, $J = 8.4$ Hz, 2H), 7.41-7.37 (m, 4H), 7.31 (t, $J = 7.2$ Hz, 2H), 7.26-7.22 (m, 1H), 6.64 (d, $J = 9.2$ Hz, 0.38H, isomer 1), 6.60 (d, $J = 9.2$ Hz, 0.62H, isomer 2), 6.49 (d, $J = 14.8$ Hz, 0.62H, isomer 2), 6.45 (d, $J = 15.6$ Hz, 0.38H, isomer 1), 5.76-5.62 (m, 1H), 5.38-5.27 (m, 1H), 2.83-2.68 (m, 2H), 2.36 (s, 0.48H, isomer 1), 2.26 (s, 0.52H, isomer 2), 1.67 (t, $J = 8.4$ Hz, 3H). $^{13}$C NMR (CDCl$_3$, 100 Hz): 144.8, 144.7, 136.8, 136.7, 135.0, 134.9, 132.2, 131.5, 129.7, 128.9, 128.8, 128.8, 128.8, 127.9, 127.8, 127.6, 126.7, 124.9, 124.0, 121.1, 121.0, 76.3, 75.6, 46.1, 40.0, 18.4, 13.4. HRMS (ESI): m/z calcd for C$_{19}$H$_{19}$OBrNa [M + Na]$^+$: 365.0517; Found: 365.0517.

Characterization of 3j:
Yellow oil; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.50 (d, $J = 8.4$ Hz, 2H), 7.44-7.40 (m, 3H), 7.19-7.16 (m, 3H), 6.90 (d, $J = 8.4$ Hz, 0.48H, isomer 1), 6.86 (d, $J = 8.4$ Hz, 0.52H, isomer 2), 6.38 (d, $J = 15.6$ Hz, 0.52H, isomer 2), 6.35 (d, $J = 15.2$ Hz, 0.48H, isomer 1), 5.78-5.64 (m, 1H), 5.42-5.31 (m, 1H), 2.85-2.70 (m, 2H), 2.39 (s, 0.40H, isomer 1), 2.34 (s, 3H), 2.30 (s, 0.60H, isomer 2), 1.71 (d, $J = 6.4$ Hz, 1.20H, isomer 1), 1.68 (d, $J = 6.8$ Hz, 1.80H, isomer 2).

$^{13}$C NMR (CDCl$_3$, 100 Hz): 144.8, 144.8, 136.3, 136.2, 135.9, 135.8, 135.7, 131.8, 131.3, 130.3, 130.3, 129.4, 127.6, 127.6, 127.5, 127.4, 126.7, 126.6, 126.1, 126.1, 125.7, 125.7, 124.9, 123.9, 120.9, 120.8, 76.3, 75.6, 46.0, 40.0, 19.9, 18.2, 13.2. HRMS (ESI): m/z calcd for C$_{20}$H$_{21}$OBrNa [M + Na]$^+$: 379.0673; Found: 379.0652.

Characterization of 3l:

Pale yellow oil; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.48 (d, $J = 8.0$ Hz, 2H), 7.39 (t, $J = 7.2$ Hz, 2H), 7.23 (t, $J = 8.4$ Hz, 1H), 6.97 (d, $J = 7.6$ Hz, 1H), 6.80 (d, $J = 8.0$ Hz, 1H), 6.61 (s, $J = 9.2$ Hz, 0.36H, isomer 1), 6.57 (d, $J = 8.8$ Hz, 0.64H, isomer 2), 6.48 (d, $J = 14.4$ Hz, 0.64H, isomer 2), 6.44 (d, $J = 16.0$ Hz, 0.36H, isomer 1), 5.76-5.62 (m, 1H), 5.37-5.26 (m, 1H), 3.81 (s, 3H), 2.83-2.68 (m, 2H), 2.38 (s, 0.60H, isomer 1), 2.27 (s, 0.40H, isomer 2), 1.67 (t, $J = 7.6$ Hz, 3H). $^{13}$C NMR (CDCl$_3$, 100 Hz): 160.0, 160.0, 144.7, 138.2, 138.2, 135.2, 135.2, 132.2, 131.5, 129.7, 129.7, 128.8, 128.7, 127.6, 127.6, 124.9, 124.0, 121.1, 121.0, 119.4, 113.5, 113.5, 112.0, 76.3, 75.5, 55.4, 46.0, 40.0, 18.4, 13.4. HRMS (ESI): m/z calcd for C$_{20}$H$_{21}$OBrNa [M + Na]$^+$: 395.0623; Found: 395.0623.

Characterization of 3w:
Pale yellow oil; \( ^1H \) NMR (CDCl\(_3\), 400 MHz) \( \delta: 7.45-7.34 \) (m, 4H), 7.19-7.17 (m, 3H), 8.59-6.44 (m, 2H), 5.76-5.62 (m, 1H), 5.36-5.25 (m, 1H), 2.85-2.63 (m, 2H), 2.35 (s, 3H), 2.35 (s, 0.25H, isomer 1), 2.23 (s, 0.75H, isomer 2), 1.67 (d, \( J = 6.8 \) Hz, 3H). \( ^{13}C \) NMR (CDCl\(_3\), 100 MHz) \( \delta: 142.6, 138.2, 138.1, 137.7, 137.6, 137.4, 137.2, 133.1, 133.1, 132.4, 131.5, 130.9, 130.9, 130.0, 129.6, 129.6, 128.7, 128.7, 126.3, 126.2, 126.1, 125.8, 125.8, 125.4, 124.5, 76.7, 75.9, 46.2, 40.2, 21.5, 18.7, 13.7. \) HRMS (ESI): m/z calcd for C\(_{20}\)H\(_{20}\)OCl\(_2\)Na [M + Na]\(^+\): 369.0789; Found: 369.0780.
\[1^H \text{NMR Spectrum (400 MHz, CDCl}_3\text{)} \] of Compound 2a
\( ^{13}\text{C} \) NMR Spectrum (100 MHz, CDCl\(_3\)) of Compound 2a

\( ^{1}\text{H} \) NMR Spectrum (400 MHz, CDCl\(_3\)) of Compound 2b
$^{13}$C NMR Spectrum (100 MHz, CDCl$_3$) of Compound 2b

$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 2c
$^{13}$C NMR Spectrum (100 MHz, CDCl$_3$) of Compound 2c

$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 2d
$^{13}$C NMR Spectrum (100 MHz, CDCl$_3$) of Compound 2d

$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 2e
$^{13}\text{C NMR Spectrum (100 MHz, CDCl}_3\text{)}$ of Compound 2e

$^1\text{H NMR Spectrum (400 MHz, CDCl}_3\text{)}$ of Compound 2f
$^{13}$C NMR Spectrum (100 MHz, CDCl$_3$) of Compound 2f

$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 2g
13C NMR Spectrum (100 MHz, CDCl3) of Compound 2g

1H NMR Spectrum (400 MHz, CDCl3) of Compound 2h
$^{13}$C NMR Spectrum (100 MHz, CDCl$_3$) of Compound 2h

$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 2i
$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 2j

$^{13}$C NMR Spectrum (100 MHz, CDCl$_3$) of Compound 2i
$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 2k
$^{13}$C NMR Spectrum (100 MHz, CDCl$_3$) of Compound 2k

$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 2l
$^{13}$C NMR Spectrum (100 MHz, CDCl$_3$) of Compound 2l

$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 2m
$^{13}$C NMR Spectrum (100 MHz, CDCl$_3$) of Compound 2m

$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 2n
$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 2o

$^{13}$C NMR Spectrum (100 MHz, CDCl$_3$) of Compound 2n
$^{13}$C NMR Spectrum (100 MHz, CDCl$_3$) of Compound 2o

$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 2p
$^{13}$C NMR Spectrum (100 MHz, CDCl$_3$) of Compound 2p

$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 2q
$^{13}$C NMR Spectrum (100 MHz, CDCl$_3$) of Compound 2q

$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 2r
$^{13}$C NMR Spectrum (100 MHz, CDCl$_3$) of Compound 2r

$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 2s
$^{13}$C NMR Spectrum (100 MHz, CDCl$_3$) of Compound 2s

$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 2t
\[ \text{C NMR Spectrum (100 MHz, CDCl}_3\text{) of Compound 2t} \]

\[ \text{H NMR Spectrum (400 MHz, CDCl}_3\text{) of Compound 2u} \]
$^{13}$C NMR Spectrum (100 MHz, CDCl$_3$) of Compound 2u

$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 2v
$^{13}$C NMR Spectrum (100 MHz, CDCl$_3$) of Compound 2v

$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of $\gamma$-Adduct from 4-Phenylbut-3-en-2-one 1s
$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 3a

Br

H

HO

$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 3a
$^{13}$C NMR Spectrum (100 MHz, CDCl$_3$) of Compound 3a

$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 3h
$^{13}$C NMR Spectrum (100 MHz, CDCl$_3$) of Compound 3h

$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 3j
$^{13}$C NMR Spectrum (100 MHz, CDCl$_3$) of Compound 3j

$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 3l
$\text{H NMR Spectrum (400 MHz, CDCl}_3$) of Compound 3w

$\text{C NMR Spectrum (100 MHz, CDCl}_3$) of Compound 3l
$^{13}$C NMR Spectrum (100 MHz, CDCl$_3$) of Compound 3w

$^1$H NMR Spectrum (400 MHz, CDCl$_3$) of Compound 4
$^{13}$C NMR Spectrum (100 MHz, CDCl$_3$) of Compound 4