Supporting Information

Di- and Triheteroaryalkanes via Self-Condensation and Intramolecular Friedel-Crafts Type Reaction of Heteroaryl alcohols

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Cross-over experiment between alcohols 6 and 11: To a 0.1 M solution of alcohol 6 (41 mg, 0.178 mmol) and alcohol 11 (30 mg, 0.178 mmol) in nitromethane was added Yb(OTf)$_3$ (0.01 equiv) at room temperature. The reaction was stirred at room temperature until the alcohols were consumed as monitored by TLC and the reaction mixture was quenched with aqueous saturated sodium bicarbonate solution (1-2 mL). Diluted the reaction mixture with ethyl acetate (1-2 mL) and the layers were separated. The aqueous layer was further extracted with ethyl acetate (1-2 mL). The organic layers were combined, dried over Na$_2$SO$_4$, concentrated. Submitted the crude reaction mixture for $^1$H-NMR and GCMS analysis.

Fig. 1 Crude $^1$H-NMR spectrum of the cross-over experiment between alcohols 6 and 11.
Fig. 2 GCMS spectrum of the crude reaction mixture of the cross-over experiment between alcohols 6 and 11.
**^1H-NMR experiment with alcohol 4:** Alcohol 4 (~15 mg) was taken in deuterated nitromethane (CD$_3$NO$_2$) in an NMR tube and Yb(OTf)$_3$ (~1 mg) was added at 20 °C. Reaction progress was monitored at an interval of 3 min at 20 °C until complete disappearance of starting compound. No trace of 2-methylfuran was identified by $^1$H-NMR analysis throughout the experiment, supporting an intramolecular version.

(Note: Conducting reaction at 20 °C under no stirring delayed the completion significantly, which is advantageous in monitoring 2-methylfuran formation).

**Intramolecular (our proposal)**

![Intramolecular Reaction](image)

**Intermolecular (proposed by Balaban and Liang)**

![Intermolecular Reaction](image)

*Fig. 3* $^1$H-NMR experiment with alcohol 4 (stacked NMRs).
Fig. 4 $^1$H-NMR experiment with alcohol 4 (stacked NMRs in another format).
**Procedure for cross-over experiment between alcohol 5 with external nucleophiles:** To a 0.1 M solution of the alcohol 5 in nitromethane were added nucleophile (1.2 equiv) followed by Yb(OTf)$_3$ (0.01 equiv) at room temperature. The reaction was stirred at room temperature until the alcohol was consumed as monitored by TLC and the reaction mixture was quenched with aqueous saturated sodium bicarbonate solution (1-2 mL). Diluted the reaction mixture with ethyl acetate (1-2 mL) and the layers were separated. The aqueous layer was further extracted with ethyl acetate (1-2 mL). The organic layers were combined, dried over Na$_2$SO$_4$, concentrated. Submitted the crude reaction mixture for $^1$H-NMR and HRMS analysis.

When nucleophile (a), (b) and (d) were employed, only 22 was obtained. When nucleophile (c) was employed, only 22d was obtained.

![Diagram](image)

**Fig. 5** Stacked crude $^1$H-NMR spectra of nucleophile cross-over experiments.
Fig. 6 HRMS spectrum of cross-over reaction between alcohol 5 and nucleophile c.

Fig. 7 HRMS spectrum of cross-over reaction between alcohol 5 and nucleophile d.
**Procedure for trapping experiment:** 0.1 M solution of alcohol 5 (50 mg) in nitromethane was taken in two necked round bottom flask (RB-1) at room temperature. RB-1 was connected to another two necked round bottom flask (RB-2) which was held at −70 °C, other neck of RB-2 was connected to the vacuum pump. In another round bottom flask (RB-3) 0.01 equiv of Yb(OTf)₃ (~2 mg) was dissolved in 0.5 mL of DCM (Yb(OTf)₃ is not soluble in nitromethane) under inert atmosphere. 0.1 mL of the DCM solution of Yb(OTf)₃ (in RB-3) was added to the alcohol solution (in RB-1) at an interval of 1-2 min under vacuum (~600 mmHg) at room temperature. The reaction mixture was stirred at room temperature until the alcohol was consumed as monitored by TLC. Residue collected in RB-2 at −70 °C was submitted for crude ¹H-NMR as in Fig-6. No trace of 2-methylfuran (B. P = 63-65 °C) was observed.

![Diagram](https://example.com/diagram.png)

**Fig. 6** Stacked ¹H-NMR spectra of the collected residue and 2-methylfuran.
Table 1S. Solvent screening results.\textsuperscript{a}

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Time (Min)</th>
<th>Yield\textsuperscript{b} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acetone</td>
<td>20</td>
<td>56</td>
</tr>
<tr>
<td>2</td>
<td>Acetonitrile</td>
<td>15</td>
<td>59</td>
</tr>
<tr>
<td>3</td>
<td>Ethylacetate</td>
<td>15</td>
<td>42</td>
</tr>
<tr>
<td>4</td>
<td>Dichloromethane</td>
<td>20</td>
<td>34</td>
</tr>
<tr>
<td>5</td>
<td>MTBE</td>
<td>10</td>
<td>56</td>
</tr>
<tr>
<td>6</td>
<td>Toluene</td>
<td>20</td>
<td>32</td>
</tr>
<tr>
<td>7</td>
<td>THF</td>
<td>10</td>
<td>34</td>
</tr>
<tr>
<td>8</td>
<td>Neat</td>
<td>3 h</td>
<td>54</td>
</tr>
<tr>
<td>9</td>
<td>Water + SDS (20 mol%)</td>
<td>48 h</td>
<td>–</td>
</tr>
<tr>
<td>10</td>
<td>Water + L-Allanine (20 mol%)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>11</td>
<td>Water + TMEDA (20 mol%)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>12</td>
<td>Brine</td>
<td>48 h</td>
<td>–</td>
</tr>
</tbody>
</table>

\textsuperscript{a} All reactions were done on 0.2 mmol scale in 0.2 M dilution.

\textsuperscript{b} Isolated yield after column chromatography.
**BiCl₃ catalyzed reactions:** For comparison, initial few reactions were performed with BiCl₃ as catalyst, which was found to be inferior compared to Yb(OTf)₃.

Scheme 1S. BiCl₃-catalyzed dimerization-fragmentation of furfuryl and thienyl alcohols.
Synthesis of furfuryl and thienyl alcohols: Furfuryl and thienyl alcohols were prepared according to literature procedures, either by the addition of organolithium reagents or organomagnesium reagents to aldehydes (for example: 5-methyl furan-2-carboxaldehyde, 5-methyl thiophene-2-carboxaldehyde, etc) or by the generation of furyllithium/ thienyllithium and addition to aldehydes (for example: isovaleraldehyde, 2-methylpentanal, benzaldehyde, acetaldehyde, etc) as in the following general scheme.

\[
\begin{align*}
\text{RCO} & \xrightarrow{\text{RMgBr or RLi}} \text{R} \xrightarrow{\text{Li}} \text{R}-\text{CHO} \\
& \xrightarrow{\text{R}-\text{CHO}} \text{R} \xrightarrow{\text{R}} \text{CHO} \\
R, R_1 &= \text{alkyl}, \text{aryl} \\
X &= \text{O, S}
\end{align*}
\]

Synthesis of indolyl and pyrrolyl alcohols: 3-Indolyl alcohols were prepared by the acylation of N-methylindole based on literature procedure by using 1.8 M solution of EtAlCl₂ in THF followed by reduction (using LiAlH₄ or NaBH₄). Alcohols were used immediately without any further purification. 3-Pyrrolyl alcohols were obtained by the reduction of N-methyl-3-acetylpyrrole by LiAlH₄.

\[
\begin{align*}
\text{RCOO} & \xrightarrow{\text{EtAlCl₂}} \text{R} \xrightarrow{\text{LiAlH₄/NaBH₄}} \text{R} \xrightarrow{\text{0°C, THF}} \\
R &= \text{alkyl}, \text{aryl}
\end{align*}
\]

2-Indolyl and 2-pyrrolyl alcohols were prepared by the addition of organolithium reagents or organomagnesium reagents to N-methylindole-2-carboxaldehyde and N-methylpyrrole-2-carboxaldehyde.

\[
\begin{align*}
\text{RCO} & \xrightarrow{\text{RMgBr or RLi}} \text{R} \xrightarrow{\text{THF, 0°C}} \\
& \xrightarrow{\text{THF, 0°C}} \text{R} \xrightarrow{\text{0°C}} \text{CHO}
\end{align*}
\]

Some of the furfuryl, thienyl, indolyl and pyrrolyl alcohols employed in this study are already known in the literature with complete characterization data. Spectroscopic data of

some important and the newly synthesized alcohols is presented below. Most of the furfuryl
and 3-indolyl alcohols employed in this study are found to be unstable and decompose upon
storage; some of them decomposed on silica gel and even in deuterated chloroform. But,
pyrrolyl and thienyl alcohols are found to be reasonably stable upon cold storage.

![Diagram](image)

1-(5-methylfuran-2-yl)pent-4-en-1-ol (7).
Pale yellow oil. R_f = 0.4 (Hexane/EtOAc = 9/1). IR (thin film, neat): v_max /cm^{-1} 3359, 2923,
1641, 1565, 1221, 1020, 784. ^1H NMR (400 MHz, CDCl_3): δ 6.03 (d, J = 3.0 Hz, 1H), 5.79
(s, 1H), 5.81-5.71 (m, 1H), 5.00-4.90 (m, 2H), 4.55 (t, J = 6.8 Hz, 1H), 2.20 (s, 3H), 2.01-
1.82 (m, 2H), 1.85 (q, J = 7.4 Hz, 2H). ^13C NMR (100 MHz, CDCl_3): δ 157.4, 151.6, 137.9,
115.0, 106.6, 105.9, 67.1, 34.4, 29.8, 13.5. HRMS (ESI-TOF): m/z calcd for C_{10}H_{13}O
(M–OH)^+: 149.0970. Found: 149.0975.

![Diagram](image)

1-(5-Methylfuran-2-yl)oct-2-yn-1-ol (8).
Pale yellow oil. R_f = 0.5 (Hexane/EtOAc = 9/1). IR (thin film, neat): v_max /cm^{-1} 3417, 2925,
1643, 1374, 1024, 1004. ^1H NMR (400 MHz, (CD_3)_2SO): δ 6.19 (d, J = 3.1 Hz, 1H), 6.00
(dd, J = 3.0 and 1.0 Hz, 1H), 5.86 (d, J = 6.3 Hz, 1H), 5.25 (dt, J = 6.3 and 2.0 Hz, 1H), 2.24
(s, 3H), 2.24-2.26 (m, 2H), 1.48-1.42 (m, 2H), 1.36-1.26 (m, 4H), 0.87 (t, J = 7.0 Hz, 3H).
^13C NMR (100 MHz, (CD_3)_2SO): δ 153.5, 151.5, 107.7, 106.6, 84.8, 80.1, 56.9, 30.8, 28.2,
22.0, 18.3, 14.3, 13.7. HRMS (ESI-TOF): m/z calcd for C_{13}H_{15}O (M–OH)^+: 189.1279.
Found: 189.1265.

2009, 351, 2469.
Cyclopropyl(5-methylfuran-2-yl)methanol (9).

Pale yellow oil. Rf = 0.5 (Hexane/EtOAc = 9/1). IR (thin film, neat): νmax /cm⁻¹ 3389, 1561, 1423, 1220, 1020, 784. ¹H NMR (400 MHz, (CD₃)₂SO): δ 6.13 (d, J = 3.0 Hz, 1H), 5.97 (dd, J = 2.5 and 1.5 Hz, 1H), 5.16 (d, J = 5.3 Hz, 1H), 3.89 (dd, J = 7.4 and 5.4 Hz, 1H), 2.23 (s, 3H), 1.19-1.10 (m, 1H), 0.50-0.34 (m, 3H), 0.26-0.20 (m, 1H).

3-(1,3-Dioxan-2-yl)-1-(5-methylfuran-2-yl)propan-1-ol (10).

Pale yellow oil. Rf = 0.5 (Hexane/EtOAc = 9/1). IR (thin film, neat): νmax /cm⁻¹ 3425, 2963, 2926, 1379, 1248, 1130, 1048, 989. ¹H NMR (400 MHz, (CD₃)₂SO): δ 6.06 (d, J = 3.0 Hz, 1H), 5.98-5.97 (m, 1H), 5.15 (d, J = 5.5 Hz, 1H), 4.59 (t, J = 5.1 Hz, 1H), 4.30-4.38 (m, 1H), 3.96 (dd, J = 10.4 and 5.2 Hz, 2H), 3.69-3.64 (m, 2H), 2.33 (s, 3H), 1.96-1.83 (m, 1H), 1.74-1.67 (m, 1H), 1.60-1.45 (m, 2H), 1.32-1.28 (m, 1H). ¹³C NMR (100 MHz, (CD₃)₂SO): δ 156.5, 150.4, 106.3, 106.2, 101.7, 66.4, 66.1 (2CH), 31.4, 30.4, 25.8, 13.7. HRMS (ESI-TOF): m/z calcd for C₁₂H₁₈O₄Na (M+Na⁺): 249.1103. Found: 249.1104.

1-(5-Ethylfuran-2-yl)-3-phenylpropan-1-ol (11).

Pale yellow oil. Rf = 0.5 (EtOAc/Hexane = 1/4). IR (thin film, neat): νmax /cm⁻¹ 3246, 2987, 1456, 1289, 768. ¹H NMR (400 MHz, (CD₃)₂SO): δ 7.29-7.26 (m, 2H), 7.20-7.15 (m, 3H), 6.13 (d, J = 3.3 Hz, 1H), 5.98-5.97 (m, 1H), 5.29 (d, J = 4.5 Hz, 1H), 4.44 (q, J = 5.9 Hz, 1H), 2.62-2.60 (m, 1H), 2.60-2.59 (m, 3H), 1.97 (q, J = 7.4 Hz, 2H), 1.16 (t, J = 7.4 Hz, 3H). ¹³C NMR (100 MHz, (CD₃)₂SO): δ 156.5, 156.1, 142.3, 128.7 (4CH), 126.1, 106.2, 104.9, 65.6, 37.8, 31.8, 21.2, 12.5. HRMS (ESI-TOF): m/z calcd for C₁₃H₁₇O (M–OH)⁺: 213.1279. Found: 213.1267.

(Furan-2-yl)(5-methylfuran-2-yl)methanol (12).
Pale yellow oil. \( R_f = 0.5 \) (Hexane/EtOAc = 9/1). IR (thin film, neat): \( \nu_{\text{max}} /\text{cm}^{-1} 3377, 2923, 1218, 1008, 777. \) \(^1\)H NMR (400 MHz, (CD\(_3\))\(_2\)SO): \( \delta \) 7.60 (dd, \( J = 1.9 \) and 0.9 Hz, 1H), 6.42 (dd, \( J = 3.4 \) and 1.6 Hz, 1H), 6.31 (dt, \( J = 3.3 \) and 0.8 Hz, 1H), 6.15 (d, \( J = 3.0 \) Hz, 1H), 6.04 (d, \( J = 5.5 \) Hz, 1H), 6.02-6.00 (m, 1H), 5.64 (d, \( J = 5.8 \) Hz, 1H), 2.21 (s, 3H). \(^{13}\)C NMR (100 MHz, (CD\(_3\))\(_2\)SO): \( \delta \) 155.4, 153.4, 151.3, 142.6, 110.7, 108.0, 107.1, 106.7, 63.0, 13.7. HRMS (ESI-TOF): \( m/z \) calcd for C\(_{10}\)H\(_9\)O\(_3\) (M–H)\(^+\): 177.0552. Found: 177.0578.

![Image](5-Methylfuran-2-yl)(5-methylthiophen-2-yl)methanol (13).

Pale yellow oil. \( R_f = 0.5 \) (Hexane/EtOAc = 9/1). IR (thin film, neat): \( \nu_{\text{max}} /\text{cm}^{-1} 3425, 2920, 1461, 1240, 1045, 1020, 789. \) \(^1\)H NMR (400 MHz, (CD\(_3\))\(_2\)SO): \( \delta \) 6.74 (d, \( J = 5.0 \) Hz, 1H), 2.46 (s, 3H), 7.80 (m, 1H), 7.53-7.45 (m, 8H), 6.69 (d, \( J = 63.5 \) Hz, CCF\(_3\)), 126.8 (q, \( J = 63.5 \) Hz, CCF\(_3\)), 126.6 (3CH), 123.0 (d, \( J = 15.3 \) Hz), 120.4 (d, \( J = 15.9 \) Hz), 109.7, 107.0, 70.2. HRMS (ESI-TOF): \( m/z \) calcd for C\(_{18}\)H\(_{12}\)F\(_3\)O (M–OH)\(^+\): 301.0840. Found: 301.0854.

![Image](5-(3-(Trifluoromethyl)phenyl)furan-2-yl)(phenyl)methanol (14).

Pale yellow oil. \( R_f = 0.5 \) (EtOAc/Hexane = 3/7). IR (thin film, neat): \( \nu_{\text{max}} /\text{cm}^{-1} 3456, 2945, 1456, 1098, 764, 567. \) \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.90 (dd, \( J = 1.5 \) and 0.8 Hz, 1H), 7.83-7.80 (m, 1H), 7.53-7.45 (m, 8H), 6.69 (d, \( J = 3.8 \) Hz, 1H), 6.23 (s, 1H), 5.94 (d, \( J = 4.5 \) Hz, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 156.3, 154.2, 152.4, 140.4, 131.3, 128.6 (q, \( J = 213.3 \) Hz, CF\(_3\)), 128.5 (3CH), 126.8 (q, \( J = 63.5 \) Hz, CCF\(_3\)), 126.6 (3CH), 123.0 (d, \( J = 15.3 \) Hz), 120.4 (d, \( J = 15.9 \) Hz), 109.7, 107.0, 70.2. HRMS (ESI-TOF): \( m/z \) calcd for C\(_{18}\)H\(_{12}\)F\(_3\)O (M–OH)\(^+\): 301.0840. Found: 301.0854.

![Image](1-(5-(3-(Trifluoromethyl)phenyl)furan-2-yl)pentan-1-ol (15).
Pale yellow oil. $R_f = 0.5$ (EtOAc/Hexane = 3/7). IR (thin film, neat): $\nu_{\text{max}} / \text{cm}^{-1}$ 3456, 2945, 1456, 1098, 764, 567. $^1$H NMR (400 MHz, (CD$_3$)$_2$CO): $\delta$ 8.01-7.98 (m, 2H), 7.65-7.59 (m, 2H), 8.70 (d, $J = 3.3$ Hz, 1H), 6.42 (dd, $J = 3.4$ Hz and 0.6 Hz, 1H), 4.73 (t, $J = 6.8$ Hz, 1H), 2.94 (br s, 1H), 2.07 (dt, $J = 4.5$ and 2.2 Hz, 2H), 1.91-1.87 (m, 4H), 0.91 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (100 MHz, (CD$_3$)$_2$CO): $\delta$ 159.3, 150.7, 132.0, 130.4 (q, $J = 63.5$ Hz, CCF$_3$), 129.7 (2CH), 125.7 (q, $J = 269.3$ Hz, CF$_3$), 123.3 (q, $J = 4.0$ Hz), 119.6 (q, $J = 3.8$ Hz), 107.5 (2CH), 66.9, 35.5, 27.6, 22.3, 13.4. HRMS (ESI-TOF): $m/z$ calcd for C$_{16}$H$_{16}$F$_2$O (M–OH)$^+$: 281.1150. Found: 281.1154.

(5-(3-Chlorophenyl)furan-2-yl)methanol (16).

Pale yellow oil. $R_f = 0.5$ (EtOAc/Hexane = 3/7). IR (thin film, neat): $\nu_{\text{max}} / \text{cm}^{-1}$ 3325, 2934, 1453, 1398, 1234, 1044, 764. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.68 (t, $J = 1.9$ Hz, 1H), 7.56 (dt, $J = 7.8$ and 1.4 Hz, 1H), 7.32-7.25 (m, 3H), 6.65 (d, $J = 3.3$ Hz, 1H), 4.7 (d, $J = 5.5$ Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 154.1, 153.5, 134.7, 132.2, 129.9, 127.3, 123.8, 121.8, 110.1, 106.8, 57.6. HRMS (ESI-TOF): $m/z$ calcd for C$_{11}$H$_8$ClO (M–OH)$^+$: 191.0263. Found: 191.0258.

(5-Methylthiophen-2-yl)(phenyl)methanol (17).

Colorless solid. M.P = 54-56 °C. $R_f = 0.5$ (hexane/EtOAc = 9/1). IR (thin film, neat): $\nu_{\text{max}} / \text{cm}^{-1}$ 3324, 1446, 1190, 1044, 763. $^1$H NMR (400 MHz, CDCl$_3$): 7.52-7.25 (m, 5H), 6.64 (s, 1H), 6.60 (s, 1H), 5.62 (s, 1H, CHOCH), 2.47 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): 143.5, 141.3, 140.4, 128.4 (2CH), 127.8, 127.1 (2CH), 125.8, 124.3, 76.2 (CHOH), 15.4. HRMS (ESI-TOF): $m/z$ calcd for C$_{12}$H$_{11}$OS (M–H)$^+$: 203.0531. Found: 203.0538.

5-Methylthiophen-2-yl(p-tolyl)methanol (18).
White solid. M.P = 42-44 °C. R_f = 0.5 (Hexane/EtOAc = 4/1). IR (thin film, neat): ν_max /cm⁻¹ 3417, 2925, 1374, 1024, 746. **¹H NMR** (400 MHz, (CD₃)₂SO): δ 7.30 (d, J = 7.2 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 6.63-6.58 (m, 2H), 6.07-6.05 (m, 1H), 5.8 (br s, 1H, OH), 2.36 (s, 3H), 2.28 (s, 3H). **¹³C NMR** (100 MHz, (CD₃)₂SO): δ 148.5, 142.5, 138.5, 136.5, 129.0 (2CH), 126.4 (2CH), 124.8, 123.9, 71.0, 21.7, 15.4. HRMS (ESI-TOF): m/z calcd for C₁₃H₁₂S (M–H₂O)⁺: 200.0659. Found: 200.0663.

![Image 19](image19.png)

**Bis(5-methylthiophen-2-yl)methanol (19).**

Pale yellow solid. M.P = 56-60 °C. R_f = 0.5 (EtOAc/Hexane = 1/4). IR (thin film, neat): ν_max /cm⁻¹ 3465, 2987, 1208, 1109, 768. **¹H NMR** (400 MHz, (CD₃)₂SO): δ 6.73-6.71 (m, 2H), 6.61 (dq, J = 3.4 and 1.1 Hz, 2H), 6.34 (d, J = 4.3 Hz, 1H), 6.00 (d, J = 4.3 Hz, 1H), 2.39 (s, 6H). **¹³C NMR** (100 MHz, (CD₃)₂SO): δ 147.3 (2C), 138.7 (2C), 124.8 (2CH), 124.1 (2CH), 67.5, 15.4 (2CH₃). HRMS (ESI-TOF): m/z calcd for C₁₁H₁₁S₂ (M–OH)⁺: 207.0302. Found: 207.0314.

![Image 20](image20.png)

**1-(5-Methylthiophen-2-yl)pentan-1-ol (20).**

Pale yellow oil. R_f = 0.5 (EtOAc/Hexane = 1/4). IR (thin film, neat): ν_max /cm⁻¹ 3246, 2987, 1456, 1289, 768. **¹H NMR** (400 MHz, CDCl₃): δ 6.76 (d, J = 3.5 Hz, 1H), 6.62-6.61 (m, 1H), 4.82 (t, J = 6.8 Hz, 1H), 2.47 (s, 3H), 1.86-1.80 (m, 2H), 1.41-1.33 (m, 4H), 0.79 (t, J = 7.0 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃): δ 146.4, 139.1, 124.5, 123.7, 70.5, 38.7, 28.0, 25.0, 15.4, 14.0. HRMS (ESI-TOF): m/z calcd for C₁₀H₁₅S (M–OH)⁺: 167.0890. Found: 167.0893.

![Image 38](image38.png)

**2-Methyl-1-(5-methylfuran-2-yl)pent-2-en-1-ol (38).**

Pale yellow oil. R_f = 0.5 (Hexane/EtOAc = 9/1). IR (thin film, neat): ν_max /cm⁻¹ 3423, 2964, 1453, 1374, 1242, 1046. **¹H NMR** (400 MHz, (CD₃)₂SO): δ 6.04 (dd, J = 3.0 Hz, 1H), 5.95 (s, 1H), 5.49 (t, J = 7.2 Hz, 1H), 5.35 (d, J = 4.8 Hz, 1H), 4.87 (d, J = 4.8 Hz, 1H), 2.21 (s,
3H), 2.04-2.07 (m, 2H), 1.51 (s, 3H), 0.95 (t, \( J = 7.5 \) Hz, 3H). \(^{13}\)C NMR (100 MHz, (CD\(_3\)\(_2\))SO): \( \delta \) 155.5, 150.3, 135.2, 127.6, 106.9, 106.4, 72.1, 20.8, 14.4, 13.7, 12.6. HRMS (ESI-TOF): \( m/z \) calcd for C\(_{11}\)H\(_{15}\)O (M–OH): 163.1122. Found: 163.1125.

![39](image)

1-(5-Ethylfuran-2-yl)-2-methylpent-2-en-1-ol (39).

Pale yellow oil. \( R_f = 0.5 \) (EtOAc/Hexane = 1/4). IR (thin film, neat): \( \nu_{\text{max}} /\text{cm}^{-1} \) 3423, 2964, 1453, 1374, 1242, 1046. \(^1\)H NMR (400 MHz, (CD\(_3\)\(_2\))SO): \( \delta \) 6.04-6.03 (m, 1H), 5.96-5.95 (m, 1H), 5.47 (tt, \( J = 7.5 \) and 1.3 Hz, 1H), 5.34 (d, \( J = 4.8 \) Hz, 1H), 4.86 (d, \( J = 4.5 \) Hz, 1H), 2.56 (dq, \( J = 7.5 \) and 0.8 Hz, 2H), 2.09-1.98 (m, 2H), 1.51 (s, 3H), 1.41 (t, \( J = 7.2 \) and 1.3 Hz, 1H), 5.34 (d, \( J = 4.8 \) Hz, 1H), 4.86 (d, \( J = 4.5 \) Hz, 1H), 2.56 (dq, \( J = 7.5 \) and 0.8 Hz, 2H), 2.09-1.98 (m, 2H), 1.51 (s, 3H), 1.41 (t, \( J = 7.5 \) Hz, 3H), 0.94 (t, \( J = 7.5 \) Hz, 3H). \(^{13}\)C NMR (100 MHz, (CD\(_3\)\(_2\))SO): \( \delta \) 156.1, 155.3, 136.7, 120.1, 106.7, 104.9, 72.1, 21.1, 20.8, 14.4, 12.7, 12.5. HRMS (ESI-TOF): \( m/z \) calcd for C\(_{12}\)H\(_{17}\)O (M–OH): 177.1279. Found: 177.1037.

![40](image)

1-(5-Ethylfuran-2-yl)-2-methylbut-2-en-1-ol (40).

Pale yellow oil. \( R_f = 0.5 \) (EtOAc/Hexane = 1/4). IR (thin film, neat): \( \nu_{\text{max}} /\text{cm}^{-1} \) 3423, 2964, 1453, 1374, 1242, 1046, 746. \(^1\)H NMR (400 MHz, (CD\(_3\)\(_2\))SO): \( \delta \) 6.05 (d, \( J = 3.0 \) Hz, 1H), 5.96 (d, \( J = 3.3 \) Hz, 1H), 5.53 (q, \( J = 6.2 \) Hz, 1H), 5.34 (d, \( J = 4.5 \) Hz, 1H), 4.87 (d, \( J = 4.8 \) Hz, 1H), 2.58-2.53 (q, \( J = 7.5 \) Hz, 2H), 1.59 (d, \( J = 6.8 \) Hz, 3H), 1.51 (s, 3H), 1.32 (t, \( J = 7.5 \) Hz, 3H), 1.32 (t, \( J = 7.5 \) Hz, 3H). \(^{13}\)C NMR (100 MHz, (CD\(_3\)\(_2\))SO): \( \delta \) 156.1, 155.3, 136.7, 120.1, 106.7, 104.9, 72.2, 21.2, 13.3, 12.5 (2CH\(_3\)). HRMS (ESI-TOF): \( m/z \) calcd for C\(_{11}\)H\(_{15}\)O (M–OH): 163.1122. Found: 163.1117.

![41](image)

1-(5-Methylfuran-2-yl)pent-2-en-1-ol (41).

Pale yellow oil. \( R_f = 0.5 \) (Hexane/EtOAc = 9/1). IR (thin film, neat): \( \nu_{\text{max}} /\text{cm}^{-1} \) 3245, 2946, 1432, 1321, 1078, 746. \(^1\)H NMR (400 MHz, (CD\(_3\)\(_2\))SO): \( \delta \) 6.05 (d, \( J = 3.1 \) Hz, 1H), 5.96-5.95 (m, 1H), 5.73 (dt, \( J = 15.4 \) and 6.0 Hz, 1H), 5.63 (dd, \( J = 15.4 \) and 5.2 Hz, 1H), 5.35 (d,
J = 5.0 Hz, 1H), 4.94 (t, J = 5.8 Hz, 1H), 2.23 (s, 3H), 2.07-2.00 (m, 2H), 0.96 (t, J = 7.28 Hz, 3H). $^{13}$C NMR (100 MHz, (CD$_3$)$_2$SO): δ 155.8, 150.7, 132.9, 130.0, 106.6, 106.5, 67.4, 25.0, 13.7, 13.7. HRMS (ESI-TOF): m/z calcd for C$_{10}$H$_{13}$O (M−OH)$^+$: 149.0966. Found: 149.0960.

**1-(5-Methylfuran-2-yl)-3-phenylprop-2-en-1-ol (42).**

Pale yellow oil. R$_f$ = 0.5 (Hexane/EtOAc = 9/1). IR (thin film, neat): $\nu_{\text{max}}$ /cm$^{-1}$ 3401, 1345, 1245, 1025, 824, 702. $^1$H NMR (400 MHz, (CD$_3$)$_2$SO): δ 7.47-7.44 (m, 2H), 7.53-7.37 (m, 2H), 6.47 (dd, J = 15.8 Hz, 1H), 6.68 (d, J = 15.9 and 6.1 Hz, 1H), 6.47 (dd, J = 15.9 and 6.1 Hz, 1H), 6.16 (d, J = 3.0 Hz, 1H), 6.01-6.00 (m, 1H), 5.66 (d, J = 5.3 Hz, 1H), 5.19 (t, J = 5.5 Hz, 1H), 2.25 (s, 3H). $^{13}$C NMR (100 MHz, (CD$_3$)$_2$SO): δ 152.2, 151.3, 136.9, 130.7, 129.9, 129.1 (2C), 138.2, 146.7, 1021, 754. $^1$H NMR (400 MHz, (CD$_3$)$_2$SO): δ 6.05-6.03 (m, 1H), 5.69-5.95 (m, 1H), 5.72 (br s, 1H), 5.34 (dd, J = 4.9 and 2.9 Hz, 1H), 4.81 (br s, 1H), 4.70 (s, 2H), 2.21 (s, 3H), 2.12-2.06 (m, 2H), 1.93-1.87 (m, 2H), 1.76-1.70 (m, 1H), 1.70 (s, 3H), 1.40-1.32 (m, 1H). $^{13}$C NMR (100 MHz, (CD$_3$)$_2$SO): δ 155.4, 150.6, 149.7, 138.5, 122.1, 109.2, 107.1, 106.5, 70.1, 41.1, 30.3, 27.5, 25.2, 21.0, 13.8. HRMS (ESI-TOF): m/z calcd for C$_{14}$H$_{13}$O (M−OH)$^+$: 197.0966. Found: 197.0958.

**$(5\text{-Methylfuran-2-yl})((S)-4\text{-}\text{(prop-1-en-2-yl)cyclohex-1-enyl})\text{methanol (43).}}$**

Pale yellow oil. R$_f$ = 0.4 (Hexane/EtOAc = 9/1). IR (thin film, neat): $\nu_{\text{max}}$ /cm$^{-1}$ 3421, 2934, 1382, 1467, 1021, 754. $^1$H NMR (400 MHz, (CD$_3$)$_2$SO): δ 6.05-6.03 (m, 1H), 5.69-5.95 (m, 1H), 5.72 (br s, 1H), 5.34 (dd, J = 4.9 and 2.9 Hz, 1H), 4.81 (br s, 1H), 4.70 (s, 2H), 2.21 (s, 3H), 2.12-2.06 (m, 2H), 1.93-1.87 (m, 2H), 1.76-1.70 (m, 1H), 1.70 (s, 3H), 1.40-1.32 (m, 1H). $^{13}$C NMR (100 MHz, (CD$_3$)$_2$SO): δ 155.4, 150.6, 149.7, 138.5, 122.1, 109.2, 107.1, 106.5, 70.1, 41.1, 30.3, 27.5, 25.2, 21.0, 13.8. HRMS (ESI-TOF): m/z calcd for C$_{13}$H$_{19}$O (M−OH)$^+$: 215.1440. Found: 215.1442.
General procedure for optimization of Lewis acid screening (Table 1): To a 0.2 M solution of the alcohol 2 in nitromethane, catalyst (mol% as mentioned) was added. The reaction was stirred until the alcohol was consumed as monitored by TLC and the reaction mixture was quenched with aqueous saturated sodium bicarbonate solution (1-2 mL). Diluted the reaction mixture with solvent (1-2 mL) and the layers were separated. The aqueous layer was further extracted with solvent (1-2 mL). The organic layers were combined, dried over Na$_2$SO$_4$, concentrated, and purified by silica gel column chromatography (hexanes to 5% EtOAc-hexanes) to afford product 3.

2-Methyl-5-((5-methylfuran-2-yl)(phenyl)methyl)furan (3).

Colorless oil. R$_f$ = 0.5 (Hexanes). IR (thin film, neat): $\nu_{\text{max}}$/cm$^{-1}$ 2921, 1603, 1561, 1383, 1218, 778. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.34-7.28 (m, 5H), 5.91-5.89 (m, 4H), 5.37 (s, 1H), 2.28 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 152.8 (2C), 151.4 (2C), 139.9, 128.4 (3C), 126.9 (2CH), 108.1 (2CH), 106.0 (2CH), 45.1, 13.6 (2CH$_3$). HRMS (ESI-TOF): m/z calcd for C$_{17}$H$_{15}$O$_2$ (M–H)$^-$: 251.1072. Found: 251.1071.

General procedure for Yb(OTf)$_3$ catalyzed fragmentation reactions of furfuryl, thienyl, indolyl and pyrrolyl alcohols (Scheme 3, Tables 2 and 3): To a 0.1 M solution of the alcohol in nitromethane and was added Yb(OTf)$_3$ (0.01 equiv) at room temperature. The reaction was stirred at room temperature until the alcohol was consumed as monitored by TLC and the reaction mixture was quenched with aqueous saturated sodium bicarbonate solution (1-2 mL). Diluted the reaction mixture with ethyl acetate (1-2 mL) and the layers were separated. The aqueous layer was further extracted with ethyl acetate (1-2 mL). The organic layers were combined, dried over Na$_2$SO$_4$, concentrated, and purified by silica gel column chromatography (hexanes to 5% ethyl acetate-hexanes) to afford products.

2-Methyl-5-(1-(5-methylfuran-2-yl)propyl)furan (21).
Colorless oil. $R_f = 0.6$ (Hexanes). IR (thin film, neat): $v_{\text{max}}/\text{cm}^{-1}$ 2932, 1563, 1452, 1219, 1020, 777. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 5.96 (d, $J = 3.0$ Hz, 2H), 5.90-5.88 (m, 2H), 3.78 (t, $J = 7.5$ Hz, 1H), 2.20 (s, 6H), 2.00 (q, $J = 7.4$ Hz, 2H), 0.86 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 153.9 (2C), 150.6 (2C), 106.1 (2CH), 105.8 (2CH), 40.6, 26.1, 13.6 (2CH$_3$), 12.1. HRMS (ESI-TOF): $m/z$ calcd for C$_{13}$H$_{15}$O$_2$ (M−H)$^+$: 203.1072. Found: 203.1070.

2-Methyl-5-(1-(5-methylfuran-2-yl)pentyl)furan (22).
Colorless oil. $R_f = 0.6$ (Hexanes). IR (thin film, neat): $v_{\text{max}}/\text{cm}^{-1}$ 2926, 1562, 1452, 106.1 (2CH), 105.8 (2CH), 40.6, 26.1, 13.6 (2CH$_3$), 12.1. HRMS (ESI-TOF): $m/z$ calcd for C$_{13}$H$_{19}$O$_2$ (M−H)$^+$: 231.1385. Found: 231.1383.

2-Methyl-5-(3-methyl-1-(5-methylfuran-2-yl)butyl)furan (23).
Colorless oil. $R_f = 0.6$ (Hexane). IR (thin film, neat): $v_{\text{max}}/\text{cm}^{-1}$ 2955, 1563, 1452, 1219, 1020, 780. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 5.95 (d, $J = 3.0$ Hz, 2H), 5.89 (dd, $J = 3.0$ and 1.0 Hz, 2H), 3.94 (t, $J = 7.7$ Hz, 1H), 2.28 (s, 6H), 2.00-1.90 (m, 2H), 1.30-1.26 (m, 4H), 0.91 (t, $J = 7.0$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 154.8 (2C), 150.5 (2C), 105.9 (2CH), 105.8 (2CH), 38.9, 32.7, 29.6, 22.5, 14.0, 13.6 (2CH$_3$). HRMS (ESI-TOF): $m/z$ calcd for C$_{15}$H$_{19}$O$_2$ (M−H)$^+$: 231.1385. Found: 231.1383.

2-Methyl-5-(1-(5-methylfuran-2-yl)pent-4-enyl)furan (24).
Colorless oil. R<sub>f</sub> = 0.6 (Hexane). IR (thin film, neat): <i>ν</i><sub>max</sub>/cm<sup>-1</sup> 2933, 2854, 1566, 1543, 1463, 1345, 1220, 1020, 748. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): <i>δ</i> 5.98 (s, 2H), 5.88 (s, 2H), 5.87-5.79 (m, 1H), 5.07-4.99 (m, 2H), 4.98 (t, <i>J</i> = 7.0 Hz, 1H), 2.28 (s, 6H), 2.09-2.50 (m, 4H).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): <i>δ</i> 153.7 (2C), 150.7 (2C), 138.0, 115.0, 106.2 (2CH), 105.9 (2CH), 38.2, 32.0, 31.4, 13.6 (2CH<sub>3</sub>). HRMS (ESI-TOF): <i>m/z</i> calcd for C<sub>15</sub>H<sub>19</sub>O<sub>2</sub>Na (M+Na+H)<sup>+</sup>: 254.1283. Found: 254.1269.

![Image](2-Methyl-5-(1-(5-methylfuran-2-yl)oct-2-ynyl)furan (25).)

2-Methyl-5-(1-(5-methylfuran-2-yl)oct-2-ynyl)furan (25).

Colorless oil. R<sub>f</sub> = 0.6 (Hexane). IR (thin film, neat): <i>ν</i><sub>max</sub>/cm<sup>-1</sup> 2956, 1648, 1559, 115.0, 106.2 (2CH), 105.9 (2CH), 38.2, 32.0, 31.4, 13.6 (2CH<sub>3</sub>). HRMS (ESI-TOF): <i>m/z</i> calcd for C<sub>18</sub>H<sub>23</sub>O<sub>2</sub>Na (M+H)<sup>+</sup>: 271.1698. Found: 271.1667.

![Image](2-(Cyclopropyl(5-methylfuran-2-yl)methyl)-5-methylfuran (26).)

2-(Cyclopropyl(5-methylfuran-2-yl)methyl)-5-methylfuran (26).

Pale yellow oil. R<sub>f</sub> = 0.7 (Hexane). IR (thin film, neat): <i>ν</i><sub>max</sub>/cm<sup>-1</sup> 3083, 3008, 2923, 1661, 1563, 1516, 1433, 1020, 967, 829, 861. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): <i>δ</i> 6.04 (d, <i>J</i> = 3.0 Hz, 2H) 5.90 (d, <i>J</i> = 3.0 Hz, 2H), 3.37 (d, <i>J</i> = 8.8 Hz, 1H), 2.27 (s, 6H), 1.37-1.27 (m, 1H), 0.62-0.57 (m, 2H), 0.34-0.30 (m, 2H).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): <i>δ</i> 153.6 (2C), 150.8 (2C), 106.3 (2CH), 105.8 (2CH), 43.2, 14.2, 13.6 (2CH<sub>3</sub>). HRMS (ESI-TOF): <i>m/z</i> calcd for C<sub>14</sub>H<sub>16</sub>O<sub>2</sub> (M)<sup>+</sup>: 216.1150. Found: 216.1156.
2-(3,3-Bis(5-methylfuran-2-yl)propyl)-1,3-dioxane (27).

Brown yellow oil. \( R_f = 0.70 \) (Hexane). IR (thin film, neat): \( \nu_{\text{max}} / \text{cm}^{-1} \) 2961, 2924, 2852, 1561, 1379, 1240, 1133, 1087, 946, 892, 783. \( ^{1} \text{H NMR} \) (400 MHz, CDCl\(_3\)): \( \delta \) 5.85 (s, 2H), 5.75 (s, 2H), 4.40 (t, \( J = 5.2 \) Hz, 1H), 4.03-3.95 (m, 2H), 3.83 (t, \( J = 7.6 \) Hz, 1H), 3.63 (dt, \( J = 12.0 \) and 2.3 Hz, 2H), 2.14 (s, 6H), 1.95- 1.96 (m, 3H), 1.52-1.51 (m, 2H), 1.26-1.27 (m, 1H). \( ^{13} \text{C NMR} \) (100 MHz, CDCl\(_3\)): \( \delta \) 152.6 (2C), 151.0 (2C), 106.8 (2CH), 105.4, 102.1 (2CH), 66.9 (2C), 38.7, 33.0, 27.4, 25.8, 13.6 (2CH\(_3\)). HRMS (ESI-TOF): \( m/z \) calcd for C\(_{17}\)H\(_{22}\)O\(_4\)Na (M+Na): 313.1410. Found: 313.1414.

2-Ethyl-5-(1-(5-ethylfuran-2-yl)-3-phenylpropyl)furan (28).

Colorless oil. \( R_f = 0.3 \) (Hexanes). IR (thin film, neat): \( \nu_{\text{max}} / \text{cm}^{-1} \) 2958, 2872, 1456, 1242, 1027. \( ^{1} \text{H NMR} \) (400 MHz, CDCl\(_3\)): \( \delta \) 7.33-7.28 (m, 2H), 7.23-7.20 (m, 2H), 5.99 (d, \( J = 3.0 \) Hz, 2H), 5.92-5.91 (m, 3H), 4.01 (t, \( J = 7.7 \) Hz, 1H), 2.67-2.61 (m, 6H), 2.34-2.28 (m, 2H), 1.25 (t, \( J = 7.5 \) Hz, 6H). \( ^{13} \text{C NMR} \) (100 MHz, CDCl\(_3\)): \( \delta \) 156.5 (2C), 153.5 (2C), 141.9, 128.5 (3CH), 128.3, 125.8, 106.1 (2CH), 104.2 (2CH), 38.4, 34.7, 33.5, 21.4 (2CH\(_2\)), 12.1 (2CH\(_3\)). HRMS (ESI-TOF): \( m/z \) calcd for C\(_{21}\)H\(_{24}\)O\(_2\) (M+H\(^{+}\)): 307.1698. Found: 307.1710.

2-((Furan-2-yl)(5-methylfuran-2-yl)methyl)-5-methylfuran (29).

Colorless oil. \( R_f = 0.6 \) (Hexane). IR (thin film, neat): \( \nu_{\text{max}} / \text{cm}^{-1} \) 2923, 1503, 1384, 1218, 1008, 777, 739, 598. \( ^{1} \text{H NMR} \) (400 MHz, CDCl\(_3\)): 7.60 (d, \( J = 3.0 \) Hz, 1H), 6.41 (dd, \( J = 3.1 \) and 1.9 Hz, 1H), 6.17-6.16 (m, 1H), 6.02 (m, 4H), 5.57 (s, 1H), 2.27 (s, 6H). \( ^{13} \text{C NMR} \) (100 MHz, CDCl\(_3\)): \( \delta \) 152.4, 151.3 (2C), 150.4 (2C), 142.7, 110.9, 108.2 (2CH), 107.5, 106.9 (2CH), 34.4, 13.7 (2CH\(_3\)). HRMS (ESI-TOF): \( m/z \) calcd for C\(_{15}\)H\(_{14}\)O\(_3\) (M\(^{+}\)): 242.0943. Found: 242.0940.
2-Methyl-5-((5-methylfuran-2-yl)(5-methylthiophen-2-yl)methyl)furan (30).

Pale yellow oil. R<sub>t</sub> = 0.7 (Hexane). IR (thin film, neat): ν<sub>max</sub> / cm<sup>-1</sup> 2920, 1446, 1240, 1045, 789. <sup>1</sup>H NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>SO): δ 6.99 (d, J = 3.0 Hz, 1H), 6.59 (s, 1H), 6.00 (s, 2H), 5.91 (s, 2H), 5.52 (s, 1H), 2.44 (s, 3H), 2.28 (s, 6H). <sup>13</sup>C NMR (100 MHz, (CD<sub>3</sub>)<sub>2</sub>SO): δ 152.3 (2C), 151.2 (2C), 140.6, 138.6, 125.8, 125.1, 108.0 (2CH), 106.8 (2CH), 42.3, 15.3, 13.7 (2CH<sub>3</sub>). HRMS (ESI-TOF): m/z calcd for C<sub>16</sub>H<sub>16</sub>O<sub>2</sub>S (M<sup>+</sup>): 272.0871. Found: 272.0873.

![Chemical structure of 30](image)

2-(3-((Trifluoromethyl)phenyl)-5-((5-((3-((Trifluoromethyl)phenyl)furan-2-yl)furanyl)(phenyl)methyl)furan (31).

Colorless oil. R<sub>t</sub> = 0.4 (Hexane). IR (thin film, neat): ν<sub>max</sub> / cm<sup>-1</sup> 2917, 1511, 1444, 1226, 798. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.87 (br s, 2H), 7.82-7.79 (m, 2H), 7.51-7.48 (m, 4H), 6.70 (d, J = 3.3 Hz, 2H), 6.21 (dd, J = 3.4 and 0.9 Hz, 2H), 5.64 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 154.6 (2C), 152.0 (2C), 138.8 (2C), 131.6 (2CH), 131.2 (q, J = 32.0 Hz , 2CCF<sub>3</sub>), 129.1 (2CH), 128.7 (2CH), 128.4 (2CH), 127.5 (2C), 126.6, 124.5 (q, J = 270.0 Hz, 2CF<sub>3</sub>), 123.6 (d, J = 3.7 Hz, 2CH), 120.3 (q, J = 3.6 Hz , 2CH), 110.7 (2CH), 107.1 (2CH), 45.2. HRMS (ESI-TOF): m/z calcd for C<sub>29</sub>H<sub>17</sub>F<sub>6</sub>O<sub>2</sub> (M−H)<sup>+</sup>: 511.1133. Found: 511.1135.

![Chemical structure of 31](image)

2-(3-((Trifluoromethyl)phenyl)-5-((5-((3-((Trifluoromethyl)phenyl)furan-2-yl)pentyl)furan (32).

Colorless oil. R<sub>t</sub> = 0.7 (Hexane). IR (thin film, neat): ν<sub>max</sub> / cm<sup>-1</sup> 2917, 1511, 1444, 1226, 798, 754, 480. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.89 (s, 2H), 7.83-7.80 (m, 2H), 7.52 (m, 4H), 6.70 (d, J = 3.3 Hz, 2H), 6.26 (dd, J = 3.4 and 0.6 Hz, 2H), 4.22 (t, J = 7.7 Hz, 1H), 2.17-2.11 (m,
2H), 1.43-1.36 (m, 4H), 0.94 (t, \(J = 7.04 \) Hz, 3H). \(^{13}\text{C} \text{NMR} \) (100 MHz, CDCl\(_3\)): \(\delta \) 155.8 (2C), 151.2 (2C), 131.6 (2C), 131.2 \((q, J = 32.0 \) Hz, 2CCF\(_3\)), 129.1 (2CH), 126.4 (2CH), 123.5 \((q, J = 271.0 \) Hz, 2CCF\(_3\)), 123.4 \((q, J = 3.7 \) Hz, 2CH), 120.1 \((q, J = 3.8 \) Hz, 2CH), 108.2 (2CH), 107.1 (2CH), 39.2, 32.8, 29.6, 22.4, 13.9. HRMS (ESI-TOF): \(m/z\) calcd for \(C_{27}H_{21}F_{6}O_{2} \) (M–H): 491.1446. Found: 491.1450.

Bis(5-(3-chlorophenyl)furan-2-yl)methane (33).
White solid. M.P = 123-126 °C. R\(_f\) = 0.5 (Hexane/EtOAc = 9/1). IR (thin film, neat): \(\nu_{\text{max}} /\text{cm}^{-1}\) 2917, 1511, 1444, 1236, 798. \(^1\text{H} \text{NMR} \) (400 MHz, CDCl\(_3\)): \(\delta \) 7.66 \((t, J = 1.9 \) Hz, 2H), 7.54 \((dt, J = 7.9 \) and 1.3 Hz, 2H), 7.33-7.30 \((m, 2H)\), 7.23-7.21 \((m, 2H)\), 6.64 \((d, J = 3.3 \) Hz, 2H), 6.26 \((dt, J = 3.3 \) and 0.9 Hz, 2H), 4.16 \((s, 2H)\). \(^{13}\text{C} \text{NMR} \) (100 MHz, CDCl\(_3\)): \(\delta \) 151.6 (2C), 151.4 (2C), 134.6 (2C), 132.5 (2CH), 129.5 (2CH), 126.9 (2CH), 123.4 (2CH), 121.5 (2C), 109.0 (2CH), 107.4 (2CH), 27.8. HRMS (ESI-TOF): \(m/z\) calcd for \(C_{21}H_{13}Cl_{2}O_{2} \) (M–H): 367.0293. Found: 367.0302.

2-Methyl-5-((5-methylthiophen-2-yl)(phenyl)methyl)thiophene (34).
Colorless oil. R\(_f\) = 0.5 (Hexane). IR (thin film, neat): \(\nu_{\text{max}} /\text{cm}^{-1}\) 2918, 1492, 1450, 1227, 795. \(^1\text{H} \text{NMR} \) (400 MHz, CDCl\(_3\)): \(\delta \) 7.34-7.28 \((m, 5H)\), 6.67-6.58 \((m, 4H)\), 5.69 \((s, 1H)\), 2.42 \((s, 6H)\). \(^{13}\text{C} \text{NMR} \) (100 MHz, CDCl\(_3\)): \(\delta \) 145.2 (2C), 143.7, 139.0, 128.4 (2CH), 128.2, 126.9, 125.6 (2CH), 124.5 (4CH), 47.6, 15.3 (2CH\(_3\)). HRMS (ESI-TOF): \(m/z\) calcd for \(C_{17}H_{16}S_{2} \) (M\(^+\)): 284.0693. Found: 284.0698.
2-Methyl-5-((5-methylthiophen-2-yl)(p-tolyl)methyl)thiophene (35).

Colorless oil. Rf = 0.7 (Hexane). IR (thin film, neat): νmax /cm⁻¹ 2917, 1511, 1444, 1226, 798, 754, 480. ¹H NMR (400 MHz, CDCl₃): δ 7.22 (d, J = 8.3 Hz, 2H), 7.14 (d, J = 7.8 Hz, 2H), 6.61-6.57 (m, 4H), 5.66 (s, 1H), 2.43 (s, 6H), 2.35 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 145.6, 140.9, 138.9, 136.5, 129.2, 128.1, 125.5 (46.61p6.57 (m, 4H), 5.66 (s, 1H), 2.43 (s, 6H), 2.35 (s, 3H). HRMS (ESI-TOF): m/z calcd for C₁₈H₃₁₇S: 297.0772. Found: 297.0786.

Tris(5-methylthiophen-2-yl)methane (36).

Colorless oil. Rf = 0.7 (Hexane). IR (thin film, neat): νmax /cm⁻¹ 2917, 1511, 1444, 1226, 798, 754, 480. ¹H NMR (400 MHz, CDCl₃): δ 6.72 (dd, J = 3.4 and 0.6 Hz, 3H), 6.60 (dq, J = 3.4 and 1.1 Hz, 3H), 5.85 (s, 1H), 2.45 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 145.0 (3C), 139.1 (3C), 125.2 (3CH), 124.0 (3CH), 43.0, 15.4 (3 CH and 1.0 Hz, 1H), 5.85 (s, 1H), 2.45 (s, 9H). HRMS (ESI-TOF): m/z calcd for C₁₆H₁₅S₃ (M–H)⁺: 303.0336. Found: 303.0352.

2-Methyl-5-(2-methyl-1-(5-methylfuran-2-yl)pent-1-en-3-yl)furan (44).

Colorless oil. Rf = 0.6 (Hexanes). IR (thin film, neat): νmax/cm⁻¹ 2962, 1450, 1220, 1021, 777. ¹H NMR (400 MHz, (CD₃)₂SO): δ 6.23 (d, J = 3.0 Hz, 1H), 6.13 (s, 1H), 6.14 (dd, J = 3.1 and 1.0 Hz, 1H), 6.04 (d, J = 3.0 Hz, 1H), 5.96 (dd, J = 3.0 Hz and 1.0 Hz, 1H), 3.29 (t, J = 7.7 Hz, 1H), 2.26 (s, 3H), 2.19 (s, 3H), 1.81-1.61 (m, 2H), 1.75 (s, 3H), 0.85 (t, J = 7.4 Hz, 3H). ¹³C NMR (100 MHz, (CD₃)₂SO): δ 155.2, 151.4, 150.6, 150.3, 136.1, 115.9, 109.4, 107.9, 106.5, 106.5 50.3, 23.8, 15.5, 13.7 (2CH₃), 12.4. HRMS (ESI-TOF): m/z calcd for C₁₆H₂₆O₂ (M)⁺: 244.1463. Found: 244.1460.

2-Ethyl-5-(1-(5-ethylfuran-2-yl)-2-methylpent-1-en-3-yl)furan (45).
Colorless oil. R\textsubscript{T} = 0.7 (Hexane). IR (thin film, neat): ν\textsubscript{\textit{max}} /cm\textsuperscript{-1} 2963, 1661, 1453, 1382, 962, 778. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 6.19 (s, 1H), 6.15 (d, J = 3.0 Hz, 1H), 6.10-6.00 (m, 1H), 5.90-5.95 (m, 1H), 5.89 (dt, J = 2.9 and 1.0 Hz, 1H), 3.31 (t, J = 6.5 Hz, 1H), 2.67 (q, J = 7.8 Hz, 2H), 2.61 (q, J = 7.1 Hz, 2H), 1.87 (s, 3H), 1.92-1.71 (m, 2H), 1.25 (t, J = 7.5 Hz, 3H), 1.21 (t, J = 7.5 Hz, 3H), 1.09 (t, J = 7.2 Hz, 3H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ 156.3, 156.1, 155.3, 151.8, 136.3, 115.8, 108.7, 105.6, 105.5, 104.0, 50.9, 24.1, 21.3 (2CH\textsubscript{2}), 15.4, 12.1, 12.1 (2CH\textsubscript{3}). HRMS (ESI-TOF): m/z calcd for C\textsubscript{18}H\textsubscript{23}O\textsubscript{2} (M–H): 271.1698. Found: 271.1710.

2-Methyl-5-(3-methyl-4-(5-methylfuran-2-yl)but-3-en-2-yl)furan (46).
Colorless oil. R\textsubscript{T} = 0.6 (Hexane). IR (thin film, neat): ν\textsubscript{\textit{max}} /cm\textsuperscript{-1} 2923, 1449, 1219, 1023, 889, 782. \textsuperscript{1}H NMR (400 MHz, (CD\textsubscript{3})\textsubscript{2}SO): δ 6.16–6.15 (m, 2H), 6.01 (s, 1H), 5.98 (dd, J = 3.0 and 1.0 Hz, 1H), 5.91 (dt, J = 3.1 and 1.0 Hz, 1H), 3.59 (q, J = 7.2 Hz, 1H), 2.68 (q, J = 7.5 Hz, 2H), 2.61 (q, J = 7.5 Hz, 2H), 1.97 (s, 3H), 1.42 (d, J = 7.0 Hz, 3H), 1.25 (t, J = 7.5 Hz, 3H), 1.22 (t, J = 7.5 Hz, 3H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ 156.6, 156.2, 156.1, 151.8, 138.1, 114.5, 108.8, 105.5, 105.4, 104.0, 42.9, 21.3 (2CH\textsubscript{2}), 17.5, 16.0, 12.1 (2CH\textsubscript{3}). HRMS (ESI-TOF): m/z calcd for C\textsubscript{17}H\textsubscript{21}O\textsubscript{2} (M–H): 257.1542 Found: 257.1560.

2-Methyl-5-(1-(5-methylfuran-2-yl)pent-2-enyl)furan (47). Minor
\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 6.21 (s, 1H), 6.09 (s, 1H), 5.95–5.94 (m, 1H), 5.91–5.88 (m, 1H), 5.76–5.70 (m, 1H), 5.62–5.58 (m, 1H), 4.68 (d, J = 7.3 Hz, 1H), 2.29 (s, 6H), 2.13–2.06 (m, 2H), 1.03 (t, J = 7.4 Hz, 3H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ 152.9 (2C), 151.1 (2C), 134.4, 126.4, 106.6 (2CH), 106.1 (2CH), 42.1, 25.3, 13.5 (2CH\textsubscript{3}), 13.4.

2-Methyl-5-(2-(5-methylfuran-2-yl)pent-1-enyl)furan (48). Major
Colorless oil. R\textsubscript{T} = 0.7 (Hexane). IR (thin film, neat): ν\textsubscript{\textit{max}} /cm\textsuperscript{-1} 2963, 1661, 1453, 1382, 962, 778. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 6.18 (s, 1H), 6.12 (d, J = 8.0 Hz, 1H), 5.95–5.94 (m, 2H), 5.91–5.88 (m, 2H), 3.34–3.32 (m, 1H), 2.31 (s, 3H), 2.28 (s, 3H), 1.94–1.83 (m, 1H), 1.76–1.65 (m, 1H), 0.96 (t, J = 7.4 Hz, 3H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ 155.6, 151.4,
calcd for C<sub>15</sub>H<sub>17</sub>O<sub>2</sub> (M–H)<sup>+</sup>: 229.1229. Found: 229.1245.

2-(Methyl-5-)-1-(5-methylfuran-2-yl)-3-phenylallylfuran (49). Minor

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.46-7.22 (m, 5H), 5.97-5.93 (m, 4H), 5.93- 5.92 (uneven triplet, 2H), 4.90 (br s, 1H), 2.31 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 152.0 (2C), 151.1 (2C), 151.4, 151.3, 141.4, 128.3 (2CH), 127.4, 126.4, 126.0, 108.7 (2CH), 107.5, 107.2, 106.1, 48.1, 13.6 (2CH<sub>3</sub>). HRMS (ESI-TOF): m/z calcd for C<sub>15</sub>H<sub>17</sub>O<sub>2</sub> (M–H)<sup>+</sup>: 277.1229. Found: 277.1244.

2-Methyl-5-(1-(5-methylfuran-2-yl)-3-phenylprop-1-en-2-yl)furan (50). Major

Pale yellow oil. R<sub>f</sub> = 0.7 (Hexane). IR (thin film, neat): ν<sub>max</sub> /cm<sup>-1</sup> 2921, 1561, 1450, 1218, 1020, 954, 699. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.46-7.22 (m, 5H), 6.50 (d, J = 2.8 Hz, 1H), 6.46 (dd, J = 15.7 and 7.6 Hz, 1H), 6.13 (d, J = 15.7 Hz, 1H), 6.08 (d, J = 3.12 Hz, 1H), 6.04 (d, J = 2.9 Hz, 1H), 5.99 (d, J = 2.9 Hz, 1H), 4.82 (d, J = 7.3 Hz, 1H), 2.31 (s, 3H), 2.28 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 154.2, 151.7, 151.4, 151.3, 141.4, 128.3 (2CH), 127.4, 127.2, 126.4, 120.0, 108.7 (2CH), 107.5, 107.2, 106.1, 48.1, 13.6 (2CH<sub>3</sub>). HRMS (ESI-TOF): m/z calcd for C<sub>15</sub>H<sub>17</sub>O<sub>2</sub> (M–H)<sup>+</sup>: 295.1698. Found: 295.1697.

2-Methyl-5-((5-methylfuran-2-yl)(4-(prop-1-en-2-yl)cyclohex-1-enyl)methyl)furan (51)

Colorless oil. R<sub>f</sub> = 0.6 (Hexane). IR (thin film, neat): ν<sub>max</sub>/cm<sup>-1</sup> 2923, 1449, 1219, 1023, 889, 782. <sup>1</sup>H NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>SO): δ 5.97-5.96 (m, 4H), 5.42 (m, 1H), 4.70-4.60 (m, 2H), 4.64 (s, 1H), 2.21 (s, 6H), 2.14-1.76 (m, 4H), 1.72 (s, 3H), 1.39-1.25 (m, 3H). <sup>13</sup>C NMR (100 MHz, (CD<sub>3</sub>)<sub>2</sub>SO): δ 155.1 (2C), 150.9 (2C), 149.8, 138.3, 123.6 (2C), 109.5 (2CH), 109.5, 106.7 (2CH), 46.0, 32.0, 27.4, 26.4, 21.2, 13.0 (2CH<sub>3</sub>). HRMS (ESI-TOF): m/z calcd for C<sub>20</sub>H<sub>23</sub>O<sub>2</sub> (M–H)<sup>+</sup>: 295.1698. Found: 295.1697.

2-Methyl-5-2-((5-methylfuran-2-yl)methylene)-5-(prop-1-en-2-yl)cyclohexyl)furan (52)
**1H NMR** (400 MHz, (CD$_3$)$_2$SO): δ 6.25 (d, $J = 3.0$ Hz, 1H), 6.11 (s, 1H), 6.09 (dd, $J = 3.0$ and 1.0 Hz, 1H), 5.95-5.93 (m, 2H), 4.70 (s, 2H), 3.69 (m, 1H), 3.20 (dt, $J = 14.2$ and 3.2 Hz, 1H), 2.27 (s, 3H), 2.21 (s, 3H), 2.14-1.72 (m, 4H), 1.70 (s, 3H), 1.39-1.28 (m, 2H).

**13C NMR** (100 MHz, (CD$_3$)$_2$SO): δ 152.1, 152.1, 151.0, 150.8, 150.2, 149.4, 114.6, 110.7, 108.0, 107.8, 106.0, 106.8, 44.0, 35.7, 30.5, 27.7, 26.4, 21.2, 13.0 (2CH$_3$).


**1-Methyl-3-(1-(1-methyl-1H-indol-3-yl)butyl)-1H-indole (60).**

Pale pink oil. $R_f$ = 0.6 (Hexane). IR (thin film, neat): $\nu_{\text{max}}$ /cm$^{-1}$ 2917, 1511, 1444, 1226, 798.

**1H NMR** (400 MHz, CDCl$_3$): δ 7.65 (m, 2H), 7.30-7.21 (m, 3H), 7.21 (dt, $J = 7.5$ and 1.0 Hz, 3H), 6.88 (s, 2H), 4.51 (t, $J = 7.4$ Hz, 1H), 3.76 (s, 6H), 2.22-2.08 (m, 2H), 1.47-1.28 (m, 2H), 0.94 (t, $J = 6.5$ Hz, 3H).

**13C NMR** (100 MHz, CDCl$_3$): δ 137.2 (2CH), 127.5 (2C), 126.1 (2C), 121.2 (4CH), 119.2 (2C), 118.3 (2CH), 109.6 (2CH), 38.6, 33.4, 32.6 (2CH$_3$), 21.5, 14.2. HRMS (ESI-TOF): $m/z$ calcd for C$_{22}$H$_{23}$N$_2$ (M–H)$^+$: 315.1861. Found: 315.1873.

**3-(Cyclopropyl(1-methyl-1H-indol-3-yl)methyl)-1-methyl-1H-indole (61).**

Colorless oil. $R_f$ = 0.4 (Hexane). IR (thin film, neat): $\nu_{\text{max}}$ /cm$^{-1}$ 2917, 1511, 1444, 1226, 798.

**1H NMR** (400 MHz, CDCl$_3$): δ 7.52 (dt, $J = 7.5$ Hz, 2H), 7.30 (m, 2H), 7.19 (ddd, $J = 8.2$, 7.1 and 1.1 Hz, 2H), 7.03-6.97 (m, 4H), 3.99 (d, $J = 8.5$ Hz, 1H), 3.76 (s, 6H), 1.62-1.52 (m,
1H), 0.65-0.61 (m, 2H), 0.41-0.37 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 137.1 (2C), 127.6 (2C), 126.7 (2CH), 121.1 (2CH), 119.9 (2CH), 118.7 (2C), 118.3 (2CH), 109.2 (2CH), 37.9, 37.7, 17.1, 4.9.
$^1\text{H}$ and $^{13}\text{C}$-NMR data of all new compounds reported in this study
Chemical Shift (ppm)

Normalized Intensity

SpinWorks 3: SE154 Carbon test

PPM 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
SpinWorks 3: SE 04 173 A

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