Supporting Information

Photoredox/Nickel Dual-Catalyzed Deaminative Cross-Electrophile for Allenylic Alkylation with Non-Activated Alkyl Katritzky Salts

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1. General Information and Materials:

For product purification by flash column chromatography, silica gel (200~300 mesh) and n-pentane were used. $^1$H NMR spectra were recorded on 400 MHz in CDCl$_3$, $^{13}$C NMR spectra were recorded on 100 MHz in CDCl$_3$. $^{19}$F NMR spectra were recorded on 376 MHz in CDCl$_3$ using TMS as internal standard. Melting points were determined on a microscopic apparatus and were uncorrected. All products were further characterized by HRMS (high-resolution mass spectra). Copies of their $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra were provided. The starting materials were purchased from Sigma-Aldrich, Acros, TCI, Admas, J&K Chemicals, Energy Chemical and used without further purification. Kessil brand 390 (± 15) nm LED was used in a reaction box equipped cooling fan to keep reaction temperature between 15 °C and 25 °C.

2. General Procedure for Photoredox/Nickel Dual-Catalyzed Deaminative Cross-Electrophile for Allenylic Alkylation:

In a 10.0 mL snap vial with Teflon cover and magnetic stirring bar the internal propargylic carbonates 1a (0.2 mmol), alkyl Katritzky salt 2a (0.4 mmol, 2.0 equiv), NiBr$_2$·dtbbpy (0.04 mmol, 20 mol %), [Ir(dtbbpy)(ppy)$_2$]PF$_6$ (0.01 mmol, 5 mol %), DIPEA (1.6 mmol, 8.0 equiv.) and 4Å MS (30 mg, 150 g/mol) were filled. After degassing with argon by syringe needle for 5 minutes and dissolving with 1.6 mL DCM and 0.4 ml DCE, the reaction mixture was stirred for 10 minutes to become clear. Then, the vial was irradiated in reactor with cooling device using a Kessil brand 390 (± 15) nm LED (50 W). The reaction progress was monitored by TLC and GC-MS analysis. After full conversion (generally 24 hours), the reaction mixture was transferred into a separating funnel and 10 mL of distilled water and 2 mL of brine were added. Then the resulting mixture was extracted with EtOAc (10 mL*2) and final combined organic layer were dried over MgSO$_4$, filtered and concentrated in vacuum. Purification of the crude product was achieved by flash column chromatography using n-pentane as eluents on silica gel.

3. Preparation of Starting Materials:

All of propargylic carbonates and alkyl Katritzky salts were synthesized according to the previous literatures, and the NMR spectroscopy and GC-MS data were in full accordance with the data in the reported literatures.$^{1,2,3}$
4. Optimization of Reaction Conditions:

a) Screening of nickel catalysis and solvents:

![Chemical Structure](image)

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<tr>
<th>Entries</th>
<th>Catalyst (20 mol%)</th>
<th>Ligand</th>
<th>PC (5 mol%)</th>
<th>Reductant (4.0 equiv)</th>
<th>Solvent</th>
<th>Yield (%)$^a$</th>
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$^a$ Isolated yield of 3a.

b) Screening of PC and light:

![Chemical Structure](image)

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<tr>
<th>Entries</th>
<th>Catalyst (20 mol%)</th>
<th>PC (5 mol%)</th>
<th>Reductant (4.0 equiv)</th>
<th>Solvent</th>
<th>Yield (%)$^a$</th>
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<td>Entries</td>
<td>Catalyst (20 mol %)</td>
<td>PC (5 mol %)</td>
<td>Reductant</td>
<td>Solvent</td>
<td>Yield (%) &lt;sup&gt;a&lt;/sup&gt;</td>
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<td>[Ir(dtbbpy)(ppy)&lt;sub&gt;2&lt;/sub&gt;]PF&lt;sub&gt;6&lt;/sub&gt;</td>
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<td>DIPEA (8.0 eq.)</td>
<td>DCM:DCE=4:1</td>
<td>69&lt;sup&gt;b&lt;/sup&gt;</td>
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</tbody>
</table>

<sup>a</sup> Isolated yield of 3<sub>a</sub>. <sup>b</sup> With 4Å MS (30 mg, 150 g/mol).
d) Control experiment:

![Experimental setup diagram]

<table>
<thead>
<tr>
<th>Entries</th>
<th>Catalyst (20 mol %)</th>
<th>PC (5 mol %)</th>
<th>Reductant</th>
<th>Solvent</th>
<th>Yield (%)^a</th>
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<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>[Ir(dtbbpy)(ppy)_2]PF_6</td>
<td>DIPEA (8.0 eq.)</td>
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<tr>
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<td>NiBr_2·dtbbpy</td>
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<td>DIPEA (8.0 eq.)</td>
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</tbody>
</table>

^a Isolated yield of 3a. ^b With no light

5. Mechanism Characterization:

a) Radical capture experiment:

![Radical capture experiment diagram]

Radical capture experiment with TEMPO revealed the involvement of a radical intermediate during the reaction process with the complete suppression of the product 3a.

![Radical capture experiment diagram with TEMPO]

The isolated 17% yield byproduct 3aa indicates the potential radical-radical coupling between dihydropyridine radical intermediate and alkyl radical.

b) UV/Vis absorption spectroscopy:

According to the result of UV/Vis absorption spectroscopy, the intermolecular EDA complex was generated by the interaction of alkyl Katritzky salt 2a with DIPEA or TEA, which could result in the formation of alkyl radical from 2a directly. Moreover, from the result of UV/Vis absorption spectroscopy, DIPEA or TEA exhibited no influence on propargylic carbonate 1a.
c) Confirmation experiments for radical from propargylic carbonates 1a:

Propargyl radical capture product 6a and two kinds of hydrogen-capturing product 6b, 6c was isolated only in the presence of both nickel catalyst and photocatalysis with DIPEA, which confirmed the involvement of hybrid propargyl-Ni(I) or allenyl-Ni(I) species.
**d) Plausible mechanism:**

A hypothetical mechanism for this regioselective cross-electrophile allenyllic alkylation was proposed here. With irradiation by 390 nm purple light, the excited-state Ir(III)* complex induced an SET process with DIPEA through a reductive quenching cycle, leading to the formation of reduced state Ir(II) complex. Then, low-valence nickel species Ni(0) underwent a single electron oxidation addition with 1a to generate a hybrid allenyl-Ni(I) intermediate, namely allenyl radical A. Meanwhile, reduction of Katritzky salt 2a (E_{1/2} = -0.93 V vs SCE) by low-valence Ir(II) (E_{1/2} = -1.51 V vs SCE) generates alkyl radical C, which then captured allenyl species A to generate the desired radical-radical coupling product 3a and Ni(I) species. Finally, a complete co-catalytic system is achieved with reduction of Ni(I) complex to Ni(0) by the low-valence Ir(II) complex. Notably, despite photocatalyst play an indispensable role in reactions, the formation of alkyl radical C from low-valent nickel intermediate or EDA complex with DIPEA could not be ruled out. Meanwhile, though the reductive reaction atmosphere, the mechanism processing reductive elimination from Ni(III) species also could not be fully ruled out.

**6. References:**


7. Characterization Data of Substrates 1a-1b, 4a-4l, 4s:

1a: colorless oil; Eluent: n-hexane/EtOAc = 50/1;

$^1$H NMR (400 MHz CDCl$_3$, δ ppm): 1.36-1.39 (t, $J = 8.0$ Hz, 3H), 1.45-1.61 (m, 1H), 1.88-2.11 (m, 5H), 2.19-2.27 (t, $J = 16.0$ Hz, 1H), 3.80 (s, 3H), 3.95-4.00 (dd, $J_1 = 8.0$ Hz; $J_2 = 16.0$ Hz, 2H), 5.37-5.39 (d, $J = 8.0$ Hz, 1H), 5.68 (s, 2H), 6.78-6.80 (d, $J = 8.0$ Hz, 2H), 7.35-7.37 (d, $J = 8.0$ Hz, 2H);

$^{13}$C NMR (100 MHz, CDCl$_3$, δ ppm): 14.4, 23.9, 24.3, 24.5, 24.6, 26.7, 27.0, 38.1, 38.2, 54.6, 63.2, 72.2, 72.3, 82.9, 83.0, 88.7, 86.8, 113.8, 114.1, 125.1, 125.3, 126.6, 126.8, 133.2, 155.0, 159.1;

HRMS (ESI) calcd for C$_{19}$H$_{22}$O$_4$ [M+H]$^+$ m/z 315.1591, found 315.1587.

1b: colorless oil; Eluent: n-hexane/EtOAc = 50/1;

$^1$H NMR (400 MHz CDCl$_3$, δ ppm): 1.45-1.58 (m, 1H), 1.88-2.24 (m, 6H), 3.77-3.80 (d, $J = 12.0$ Hz, 6H), 5.37-5.39 (t, $J = 4.0$ Hz, 1H), 5.69 (s, 2H), 6.30-6.32 (d, $J = 8.0$ Hz, 2H), 7.36-7.38 (d, $J = 8.0$ Hz, 2H);

$^{13}$C NMR (100 MHz, CDCl$_3$, δ ppm): 23.4, 24.4, 24.5, 24.6, 26.7, 27.1, 38.1, 38.3, 54.7, 55.3, 72.3, 72.4, 76.7, 77.0, 77.3, 83.0, 83.1, 86.7, 86.8, 113.7, 114.0, 125.2, 125.4, 126.7, 126.8, 133.2, 155.1, 159.8;

HRMS (ESI) calcd for C$_{18}$H$_{20}$O$_4$ [M+H]$^+$ m/z 301.1440, found 301.1439.

4a: colorless oil; Eluent: n-hexane/EtOAc = 50/1;

$^1$H NMR (400 MHz CDCl$_3$, δ ppm): 1.09 (s, 9H), 2.31 (s, 3H), 3.79 (s, 3H), 5.18 (s, 1H), 7.07-7.09 (d, $J = 8.0$ Hz, 2H), 7.31-7.33 (d, $J = 8.0$ Hz, 2H);

$^{13}$C NMR (100 MHz, CDCl$_3$, δ ppm): 21.2, 25.4, 35.5, 54.6, 76.6, 84.0, 86.6, 119.1, 128.8, 131.6, 138.5, 155.2;

HRMS (ESI) calcd for C$_{16}$H$_{20}$O$_3$ [M+H]$^+$ m/z 261.1485, found 261.1479.

4b: colorless oil; Eluent: n-hexane/EtOAc = 50/1;
\textbf{H NMR} (400 MHz CDCl$_3$, \(\delta\) ppm): 0.89-0.92 (t, \(J = 8.0\) Hz, 3H), 1.09 (s, 9H), 1.57-1.63 (dd, \(J_1 = 8.0\) Hz; \(J_2 = 16.0\) Hz, 2H), 2.53-2.57 (t, \(J = 8.0\) Hz, 2H), 3.80 (s, 3H), 5.18 (s, 1H), 7.08-7.10 (d, \(J = 8.0\) Hz, 2H), 7.34-7.36 (d, \(J = 8.0\) Hz, 2H);

\textbf{13C NMR} (100 MHz, CDCl$_3$, \(\delta\) ppm): 13.5, 24.2, 25.4, 35.5, 37.8, 54.7, 76.6, 84.0, 86.7, 119.4, 128.3, 131.6, 143.3, 155.3;

\textbf{HRMS} (ESI) calcd for C$_{18}$H$_{24}$O$_3$ [M+H]$^+$ m/z 289.1804, found 289.1800.

4c: colorless oil; Eluent: n-hexane/EtOAc = 50/1;

\textbf{H NMR} (400 MHz CDCl$_3$, \(\delta\) ppm): 0.86-0.90 (t, \(J = 8.0\) Hz, 3H), 1.09 (s, 9H), 1.28-1.33 (m, 4H) 1.57-1.61 (t, \(J = 8.0\) Hz, 2H), 2.56-2.60 (t, \(J = 8.0\) Hz, 2H), 3.82 (s, 3H), 5.17 (s, 1H), 7.10-7.12 (d, \(J = 8.0\) Hz, 2H), 7.35-7.37 (d, \(J = 8.0\) Hz, 2H);

\textbf{13C NMR} (100 MHz, CDCl$_3$, \(\delta\) ppm): 13.8, 22.5, 25.6, 31.0, 34.6, 35.6, 54.9, 76.7, 84.1, 86.8, 119.5, 128.3, 131.8, 143.8, 155.4;

\textbf{HRMS} (ESI) calcd for C$_{20}$H$_{28}$O$_3$ [M+H]$^+$ m/z 317.2117, found 317.2113.

4d: colorless oil; Eluent: n-hexane/EtOAc = 50/1;

\textbf{H NMR} (400 MHz CDCl$_3$, \(\delta\) ppm): 1.09 (s, 9H), 1.29 (s, 9H), 3.81 (s, 3H), 5.18 (s, 1H), 7.30-7.32 (d, \(J = 8.0\) Hz, 2H), 7.37-7.39 (d, \(J = 8.0\) Hz, 2H);

\textbf{13C NMR} (100 MHz, CDCl$_3$, \(\delta\) ppm): 25.5, 31.0, 34.6, 35.6, 54.7, 76.7, 84.1, 86.6, 119.3, 125.1, 131.5, 151.7, 155.3;

\textbf{HRMS} (ESI) calcd for C$_{19}$H$_{26}$O$_3$ [M+H]$^+$ m/z 303.1960, found 303.1956.

4e: colorless oil; Eluent: n-hexane/EtOAc = 50/1;

\textbf{H NMR} (400 MHz CDCl$_3$, \(\delta\) ppm): 1.09 (s, 9H), 1.38-1.41 (t, \(J = 4.0\) Hz, 3H), 3.81 (s, 3H), 3.98-4.03 (dd, \(J_1 = 8.0\) Hz; \(J_2 = 16.0\) Hz, 2H), 5.17 (s, 1H), 6.79-6.81 (d, \(J = 8.0\) Hz, 2H), 7.35-7.38 (d, \(J = 12.0\) Hz, 2H);

\textbf{13C NMR} (100 MHz, CDCl$_3$, \(\delta\) ppm): 14.6, 25.5, 35.6, 54.8, 63.4, 76.7, 83.2, 86.6, 114.2, 114.3, 133.3, 155.4, 159.2;

\textbf{HRMS} (ESI) calcd for C$_{17}$H$_{22}$O$_4$ [M+H]$^+$ m/z 291.1596, found 291.1594.
4f: colorless oil; Eluent: *n*-hexane/EtOAc = 50/1;

$^1$H NMR (400 MHz CDCl$_3$, $\delta$ ppm): 1.11 (s, 9H) 3.83 (s, 3H), 5.20 (s, 1H), 7.33-7.37 (t, $J = 8.0$ Hz, 1H), 7.41-7.45 (t, $J = 8.0$ Hz, 2H), 7.50-7.58 (m, 6H);

$^{13}$C NMR (100 MHz CDCl$_3$, $\delta$ ppm): 25.6, 35.7, 54.9, 76.7, 85.4, 86.5, 121.2, 126.9, 127.0, 127.7, 128.8, 132.3, 140.3, 141.3, 155.4;

HRMS (ESI) calcd for C$_{21}$H$_{22}$O$_3$ [M+H]$^+$ m/z 323.1647, found 323.1647.

4g: colorless oil; Eluent: *n*-hexane/EtOAc = 50/1;

$^1$H NMR (400 MHz CDCl$_3$, $\delta$ ppm): 1.09 (s, 9H), 3.83 (s, 3H), 5.16 (m, 1H), 6.98-7.02 (t, $J = 8.0$ Hz, 2H), 7.41-7.44 (m, 2H);

$^{13}$C NMR (100 MHz CDCl$_3$, $\delta$ ppm): 25.5, 35.6, 54.9, 76.6, 84.5, 85.5, 115.4-115.6 (d, $J = 12.0$ Hz), 118.4 (d, $J = 4.0$ Hz), 133.7-133.8 (d, $J = 9.0$ Hz), 155.4, 161.4, 163.9;

$^{19}$F NMR (376 MHz CDCl$_3$, $\delta$ ppm): -110.4 (s, 1F);

HRMS (ESI) calcd for C$_{15}$H$_{17}$FO$_3$ [M+H]$^+$ m/z 265.1240, found 265.1238.

4h: colorless oil; Eluent: *n*-hexane/EtOAc = 50/1;

$^1$H NMR (400 MHz CDCl$_3$, $\delta$ ppm): 1.09 (s, 9H), 3.83 (s, 3H), 5.16 (s, 1H), 7.27-7.29 (d, $J = 8.0$ Hz, 2H), 7.36-7.38 (d, $J = 8.0$ Hz, 2H);

$^{13}$C NMR (100 MHz CDCl$_3$, $\delta$ ppm): 25.5, 35.6, 54.9, 76.5, 85.5, 85.8, 120.8, 128.5, 133.1, 134.6, 155.3;

HRMS (ESI) calcd for C$_{15}$H$_{17}$ClO$_3$ [M+H]$^+$ m/z 281.0944, found 281.0942.

4i: colorless oil; Eluent: *n*-hexane/EtOAc = 50/1;

$^1$H NMR (400 MHz CDCl$_3$, $\delta$ ppm): 1.10 (s, 9H), 3.83 (s, 3H), 5.16 (m, 1H), 7.01-7.05 (t, $J = 8.0$ Hz, 1H), 7.13-7.15 (d, $J = 8.0$ Hz, 1H), 7.23-7.30 (m, 2H);

$^{13}$C NMR (100 MHz CDCl$_3$, $\delta$ ppm): 25.5, 35.6, 55.0, 76.5, 76.7, 77.0, 77.3, 85.4 (d, $J = 4.0$ Hz), 85.4, 85.8, 115.9, 116.1, 118.6, 124.1, 124.2, 127.2, 127.8, 129.8, 129.9, 155.4, 161.0, 163.5;

$^{19}$F NMR (376 MHz CDCl$_3$, $\delta$ ppm): -112.9 (s, 1F);

HRMS (ESI) calcd for C$_{15}$H$_{17}$FO$_3$ [M+H]$^+$ m/z 265.1240, found 265.1236.
4j: colorless oil; Eluent: *n*-hexane/EtOAc = 50/1;

$^1$H NMR (400 MHz CDCl₃, δ ppm): 1.10 (s, 9H), 3.82 (s, 3H), 5.17 (s, 1H), 7.20-7.24 (t, $J = 8.0$ Hz, 1H), 7.28-7.30 (t, $J = 12.0$ Hz, 2H), 7.42 (s, 1H);

$^{13}$C NMR (100 MHz, CDCl₃, δ ppm): 25.4, 35.5, 54.8, 76.3, 85.1, 86.0, 123.9, 128.8, 129.4, 129.8, 131.6, 134.0, 155.2;

HRMS (ESI) calcd for C₃₁H₂₇ClO₃ [M+H]$^+$ m/z 281.0944, found 281.0942.

4k: colorless oil; Eluent: *n*-hexane/EtOAc = 50/1;

$^1$H NMR (400 MHz CDCl₃, δ ppm): 1.07-1.11 (dd, $J_1 = 4.0$ Hz; $J_2 = 12.0$ Hz, 6H), 2.10-2.18 (m, 1H), 3.82 (s, 3H), 5.28-5.29 (d, $J = 4.0$ Hz, 1H), 6.98-7.02 (t, $J = 8.0$ Hz, 2H), 7.41-7.44 (dd, $J_1 = 4.0$ Hz; $J_2 = 8.0$ Hz, 2H);

$^{13}$C NMR (100 MHz, CDCl₃, δ ppm): 17.5, 18.1, 32.7, 54.8, 73.5, 84.3, 85.6, 115.4-115.6 (d, $J = 22.0$ Hz), 118.3 (d, $J = 3.0$ Hz), 133.7-133.8 (d, $J = 9.0$ Hz), 155.1, 161.4, 163.9;

$^{19}$F NMR (376 MHz, CDCl₃, δ ppm): -110.3 (s, 1F);

HRMS (ESI) calcd for C₁₄H₁₁FO₃ [M+H]$^+$ m/z 251.1083, found 251.1081.

4l: colorless oil; Eluent: *n*-hexane/EtOAc = 50/1;

$^1$H NMR (400 MHz CDCl₃, δ ppm): 0.90-0.93 (t, $J = 4.0$ Hz, 3H), 0.97-0.99 (d, $J = 8.0$ Hz, 3H), 1.20-1.29 (m, 1H), 1.39-1.44 (m, 1H), 1.60-1.65 (m, 5H), 1.67-1.70 (m, 3H), 1.73-1.76 (m, 2H), 1.88-2.04 (m, 3H), 2.55-2.59 (t, $J = 8.0$ Hz, 2H), 3.81 (s, 3H), 5.08-5.11 (t, $J = 8.0$ Hz, 1H), 5.49-5.54 (m, 1H), 7.10-7.12 (d, $J = 8.0$ Hz, 2H), 7.34-7.36 (d, $J = 8.0$ Hz, 2H);

$^{13}$C NMR (100 MHz, CDCl₃, δ ppm): 13.7, 17.6, 19.4, 19.4, 24.3, 25.2, 25.3, 25.7, 29.0, 29.2, 36.8, 36.9, 37.9, 41.8, 42.2, 54.8, 67.4, 67.8, 85.2, 85.2, 86.2, 86.5, 119.4, 124.4, 128.4, 131.4, 131.7, 131.8, 143.5, 155.0, 155.1;

HRMS (ESI) calcd for C₂₃H₂₃O₃ [M+H]$^+$ m/z 357.2430, found 357.2427.
8. Characterization Data of Products 3a-3n:

\[ \text{3a, } 79\% \text{, d.r. = 1:1} \]

3a: yield 79%. According to General Procedure; colorless oil; Eluent: n-hexane/EtOAc = 200/1;
1H NMR (400 MHz CDCl₃, δ ppm): 1.13-1.21 (m, 3H), 1.25-1.34 (m, 2H), 1.38-1.42 (t, J = 8.0 Hz, 3H), 1.43-1.49 (m, 1H), 1.69-1.79 (m, 3H), 1.88-1.96 (m, 4H), 2.09-2.10 (m, 2H), 2.17-2.21 (m, 1H), 2.34-2.40 (dt, J₁ = 4.0 Hz, J₂ = 12.0 Hz, 2H), 3.99-4.04 (q, J = 8.0 Hz, 2H), 5.56 (s, 1H), 5.67 (s, 2H), 6.82-6.84 (d, J = 8.0 Hz, 2H), 7.28-7.30 (d, J = 8.0 Hz, 2H);
13C NMR (100 MHz, CDCl₃, δ ppm): 14.9, 25.1, 25.2, 26.4, 26.7, 26.8, 29.1, 29.1, 31.3, 31.5, 32.8, 32.9, 33.3, 33.3, 34.0, 37.8, 63.4, 100.2, 100.3, 112.6, 114.4, 114.4, 126.3, 126.3, 126.8, 127.2, 129.3, 129.3, 157.6, 201.6, 201.6;
HRMS (ESI) calcd for C₂₃H₃₀O [M+H]⁺ m/z 323.2375, found 323.2379.

\[ \text{3b, } 67\% \]

3b: yield 67%. According to General Procedure; colorless oil; Eluent: n-hexane/EtOAc = 200/1;
1H NMR (400 MHz CDCl₃, δ ppm): 1.07-1.35 (m, 5H), 1.67-1.84 (m, 5H), 2.31-2.34 (dt, J₁ = 4.0 Hz, J₂ = 12.0 Hz, 2H), 2.39-2.45 (dt, J₁ = 8.0 Hz, J₂ = 16.0 Hz, 2H), 2.76-2.79 (t, J = 8.0 Hz, 2H), 3.79 (s, 3H), 5.49-5.52 (dt, J₁ = 4.0 Hz, J₂ = 8.0 Hz, 1H), 6.81-6.83 (d, J = 8.0 Hz, 2H), 7.19-7.21 (m, 5H), 7.24-7.28 (dt, J₁ = 8.0 Hz, J₂ = 12.0 Hz, 2H);
13C NMR (100 MHz, CDCl₃, δ ppm): 26.4, 26.7, 26.7, 31.2, 32.8, 33.1, 35.6, 37.9, 55.3, 94.2, 111.8, 113.8, 125.8, 127.4, 128.3, 128.6, 129.4, 141.9, 158.2, 202.9;
HRMS (ESI) calcd for C₂₄H₂₈O [M+H]⁺ m/z 333.2218, found 333.2217.

\[ \text{3c, } 57\% \]

3c: yield 57%. According to General Procedure; colorless oil; Eluent: n-hexane/EtOAc = 200/1;
1H NMR (400 MHz CDCl₃, δ ppm): 0.86-0.90 (t, J = 8.0 Hz, 3H), 1.11-1.37 (m, 9H), 1.44-1.46 (m, 2H), 1.69-1.88 (m, 5H), 2.05-2.10 (dd, J₁ = 8.0 Hz, J₂ = 16.0 Hz, 2H), 2.33-2.39 (dt, J₁ = 4.0 Hz, J₂ = 12.0 Hz, 1H), 3.79 (s, 3H), 5.45-5.50 (dt, J₁ = 4.0 Hz, J₂ = 8.0 Hz, 1H), 6.84-6.86 (d, J = 8.0 Hz, 2H), 7.29-7.31 (d, J = 8.0 Hz, 2H);
13C NMR (100 MHz, CDCl₃, δ ppm): 14.1, 22.5, 26.5, 26.7, 26.8, 29.0, 29.3, 31.5, 32.8, 33.2, 37.9, 55.3, 95.0, 111.3, 113.7, 127.4, 129.7, 158.1, 202.8;
HRMS (ESI) calcd for C₂₁H₃₈O [M+H]⁺ m/z 299.2375, found 299.2374.
3d: yield 60%. According to General Procedure; colorless oil; Eluent: n-hexane/EtOAc = 200/1;

$^1$H NMR (400 MHz CDCl$_3$, δ ppm): 0.86-0.89 (t, $J = 8.0$ Hz, 3H), 1.14-1.37 (m, 11H), 1.43-1.47 (m, 2H), 1.69-1.88 (m, 5H), 2.05-2.10 (dd, $J_1 = 8.0$ Hz, $J_2 = 16.0$ Hz, 2H), 2.33-2.39 (dt, $J_1 = 4.0$ Hz, $J_2 = 12.0$ Hz, 1H), 3.79 (s, 3H), 5.45-5.50 (dt, $J_1 = 4.0$ Hz, $J_2 = 8.0$ Hz, 1H), 6.84-6.86 (d, $J = 8.0$ Hz, 2H), 7.29-7.31 (d, $J = 8.0$ Hz, 2H);

$^{13}$C NMR (100 MHz, CDCl$_3$, δ ppm): 14.1, 22.7, 26.5, 26.7, 26.8, 29.0, 29.3, 29.4, 31.7, 32.9, 33.2, 37.9, 55.3, 95.0, 111.3, 113.7, 127.4, 129.7, 158.2, 202.8;

HRMS (ESI) calcd for C$_{22}$H$_{32}$O [M+H]$^+$ m/z 313.2531, found 313.2526.

3e: yield 41%. According to General Procedure; colorless oil; Eluent: n-hexane/EtOAc = 200/1;

$^1$H NMR (400 MHz CDCl$_3$, δ ppm): 0.86-0.89 (t, $J = 8.0$ Hz, 3H), 1.14-1.36 (m, 17H), 1.41-1.46 (m, 2H), 1.69-1.88 (m, 5H), 2.05-2.10 (dd, $J_1 = 8.0$ Hz, $J_2 = 16.0$ Hz, 2H), 2.33-2.39 (dt, $J_1 = 4.0$ Hz, $J_2 = 12.0$ Hz, 1H), 3.80 (s, 3H), 5.45-5.49 (dt, $J_1 = 4.0$ Hz, $J_2 = 8.0$ Hz, 1H), 6.84-6.86 (d, $J = 8.0$ Hz, 2H), 7.29-7.31 (d, $J = 8.0$ Hz, 2H);

$^{13}$C NMR (100 MHz, CDCl$_3$, δ ppm): 14.1, 22.7, 26.5, 26.7, 26.8, 29.0, 29.3, 29.4, 29.5, 29.6, 31.9, 32.9, 33.2, 37.9, 55.3, 95.0, 111.3, 113.7, 127.4, 129.7, 158.2, 202.8;

HRMS (ESI) calcd for C$_{25}$H$_{38}$O [M+H]$^+$ m/z 355.2995, found 355.2985.

3f: yield 45%. According to General Procedure; colorless oil; Eluent: n-hexane/EtOAc = 100/1;

$^1$H NMR (400 MHz CDCl$_3$, δ ppm): 0.94-0.97 (m, 6H), 1.15-1.26 (m, 3H), 1.30-1.40 (m, 2H), 1.69-1.79 (m, 4H), 1.86-1.89 (d, $J = 12.0$ Hz, 2H), 1.97-2.01 (dt, $J_1 = 4.0$ Hz, $J_2 = 8.0$ Hz, 2H), 2.33-2.39 (dt, $J_1 = 4.0$ Hz, $J_2 = 12.0$ Hz, 1H), 3.79 (s, 3H), 5.41-5.45 (dt, $J_1 = 4.0$ Hz, $J_2 = 8.0$ Hz, 1H), 6.84-6.86 (d, $J = 8.0$ Hz, 2H), 7.29-7.31 (d, $J = 8.0$ Hz, 2H);

$^{13}$C NMR (100 MHz, CDCl$_3$, δ ppm): 22.5, 22.5, 26.5, 26.7, 26.8, 28.8, 32.8, 33.2, 38.0, 39.0, 55.3, 93.6, 110.7, 113.7, 127.4, 129.7, 158.1, 203.3;

HRMS (ESI) calcd for C$_{20}$H$_{28}$O [M+H]$^+$ m/z 285.2218, found 285.2225.
3g: yield 63%. According to **General Procedure**: colorless oil; Eluent: *n*-hexane/EtOAc = 200/1; 

**1H NMR** (400 MHz CDCl$_3$, δ ppm): 0.96 (s, 9H), 1.16-1.24 (m, 3H), 1.30-1.40 (m, 2H), 1.68-1.89 (m, 5H), 2.00-2.02 (d, $J = 8.0$ Hz, 2H), 2.33-2.39 (dt, $J_1 = 4.0$ Hz, $J_2 = 12.0$ Hz, 1H), 3.79 (s, 3H), 5.43-5.46 (t, $J = 8.0$ Hz, 1H), 6.84-6.86 (d, $J = 8.0$ Hz, 2H), 7.29-7.31 (d, $J = 8.0$ Hz, 2H);

**13C NMR** (100 MHz, CDCl$_3$, δ ppm): 26.5, 26.7, 26.8, 29.4, 31.1, 32.9, 33.2, 38.0, 44.5, 55.3, 91.8, 110.1, 113.7, 127.4, 129.7, 158.1, 203.9;

**HRMS** (ESI) calcd for C$_{21}$H$_{30}$O [M+H]$^+$ m/z 299.2375, found 299.2377.

3h: yield 41%. According to **General Procedure**: colorless oil; Eluent: *n*-hexane/EtOAc = 200/1; 

**1H NMR** (400 MHz CDCl$_3$, δ ppm): 1.11-1.36 (m, 15H), 1.41-1.46 (m, 2H), 1.69-1.87 (m, 5H), 2.00-2.10 (m, 4H), 2.33-2.39 (dt, $J_1 = 4.0$ Hz, $J_2 = 12.0$ Hz, 1H), 3.79 (s, 3H), 4.91-5.01 (m, 2H), 5.43-5.46 (dt, $J_1 = 4.0$ Hz, $J_2 = 12.0$ Hz, 1H), 5.76-5.86 (m, 1H), 6.84-6.86 (d, $J = 8.0$ Hz, 2H), 7.28-7.30 (d, $J = 8.0$ Hz, 2H);

**13C NMR** (100 MHz, CDCl$_3$, δ ppm): 26.5, 26.7, 26.8, 29.0, 29.1, 29.3, 29.3, 29.4, 29.4, 29.5, 32.9, 33.2, 33.8, 37.9, 55.3, 95.0, 111.3, 113.7, 114.1, 127.4, 129.7, 139.2, 158.2, 202.8;

**HRMS** (ESI) calcd for C$_{26}$H$_{38}$O [M+H]$^+$ m/z 367.2995, found 367.2990.

3i: yield 31%. According to **General Procedure**: colorless oil; Eluent: *n*-hexane/EtOAc = 200/1; 

**1H NMR** (400 MHz CDCl$_3$, δ ppm): 1.09-1.25 (m, 3H), 1.31-1.41 (m, 2H), 1.58-1.63 (m, 2H), 1.69-1.87 (m, 7H), 2.09-2.14 (dd, $J_1 = 8.0$ Hz, $J_2 = 16.0$ Hz, 2H), 2.34-2.40 (dt, $J_1 = 4.0$ Hz, $J_2 = 12.0$ Hz, 1H), 3.51-3.54 (t, $J = 8.0$ Hz, 2H), 3.80 (s, 3H), 5.45-5.48 (d, $J = 8.0$ Hz, 1H), 6.84-6.86 (d, $J = 8.0$ Hz, 2H), 7.27-7.30 (d, $J = 12.0$ Hz, 2H);

**13C NMR** (100 MHz, CDCl$_3$, δ ppm): 26.4, 26.5, 26.7, 26.7, 28.6, 32.2, 32.9, 33.2, 38.0, 44.9, 55.3, 94.2, 111.8, 113.8, 127.4, 129.4, 158.3, 202.9;

**HRMS** (ESI) calcd for C$_{20}$H$_{27}$ClO [M+H]$^+$ m/z 319.1823, found 319.1816.
3j: yield 61%. According to **General Procedure**: colorless oil; Eluent: n-hexane/EtOAc = 200/1;

**1H NMR** (400 MHz CDCl₃, δ ppm): 1.06-1.07 (d, J = 4.0 Hz, 6H), 1.13-1.26 (m, 3H), 1.31-1.41 (m, 2H), 1.69-1.79 (m, 3H), 1.85-1.91 (t, J = 12.0 Hz, 2H), 2.35-2.43 (m, 2H), 3.79 (s, 3H), 5.50-5.52 (dd, J₁ = 4.0 Hz, J₂ = 8.0 Hz, 1H), 6.84-6.86 (d, J = 8.0 Hz, 2H), 7.30-7.32 (d, J = 8.0 Hz, 2H);

**13C NMR** (100 MHz, CDCl₃, δ ppm): 22.6, 22.7, 26.5, 26.7, 26.8, 32.9, 33.3, 37.9, 55.3, 102.4, 112.5, 113.8, 127.2, 129.7, 158.2, 201.0;

**HRMS** (ESI) calcd for C₁₉H₂₆O [M+K]⁺ m/z 309.16, found 309.1619.

3k: yield 53%. According to **General Procedure**: colorless oil; Eluent: n-hexane/EtOAc = 200/1;

**1H NMR** (400 MHz CDCl₃, δ ppm): 0.88-0.92 (t, J = 8.0 Hz, 3H), 1.03-1.05 (m, 3H), 1.11-1.25 (m, 3H), 1.31-1.40 (m, 6H), 1.69-1.79 (m, 3H), 1.85-1.91 (t, J = 12.0 Hz, 2H), 2.21-2.25 (m, 1H), 2.34-2.40 (dt, J₁ = 4.0 Hz, J₂ = 8.0 Hz, 1H), 3.79 (s, 3H), 5.44-5.48 (dd, J₁ = 4.0 Hz, J₂ = 8.0 Hz, 1H), 6.84-6.86 (d, J = 8.0 Hz, 2H), 7.30-7.32 (d, J = 8.0 Hz, 2H);

**13C NMR** (100 MHz, CDCl₃, δ ppm): 14.2, 20.4, 20.5, 20.6, 26.5, 26.7, 26.8, 32.9, 33.3, 33.3, 33.7, 33.8, 37.9, 37.9, 39.6, 39.7, 55.3, 101.2, 101.3, 112.0, 113.7, 113.7, 127.3, 127.3, 129.7, 158.1, 201.5, 201.5;

**HRMS** (ESI) calcd for C₂₁H₃₀O [M+H]⁺ m/z 337.19, found 337.1934.

3l: yield 55%. According to **General Procedure**: colorless oil; Eluent: n-hexane/EtOAc = 200/1;

**1H NMR** (400 MHz CDCl₃, δ ppm): 1.11-1.37 (m, 10H), 1.63-1.91 (m, 10H), 2.01-2.08 (m, 1H), 2.33-2.39 (m, 1H), 3.79 (s, 3H), 5.47-5.48 (d, J = 4.0 Hz, 1H), 6.84-6.86 (d, J = 8.0 Hz, 2H), 7.30-7.32 (d, J = 8.0 Hz, 2H);

**13C NMR** (100 MHz, CDCl₃, δ ppm): 26.2, 26.2, 26.5, 26.7, 26.8, 32.9, 33.3, 33.4, 33.4, 37.8, 38.1, 55.3, 101.0, 112.1, 113.8, 127.2, 129.7, 158.1, 201.5;

**HRMS** (ESI) calcd for C₂₂H₃₂O [M+H]⁺ m/z 311.2375, found 311.2377.
3m: yield 65%. According to General Procedure; colorless oil; Eluent: n-hexane/EtOAc = 200/1; 
$^1$H NMR (400 MHz CDCl$_3$, δ ppm): 1.10 (s, 9H), 1.14-1.25 (m, 3H), 1.31-1.41 (m, 2H), 1.70-1.79 (m, 3H), 1.85-1.93 (t, $J = 16.0$ Hz, 2H), 2.34-2.41 (dt, $J_1 = 4.0$ Hz, $J_2 = 12.0$ Hz, 1H), 3.79 (s, 3H), 5.48 (m, 1H), 6.84-6.86 (d, $J = 8.0$ Hz, 2H), 7.30-7.32 (d, $J = 8.0$ Hz, 2H); 
$^{13}$C NMR (100 MHz CDCl$_3$, δ ppm): 26.5, 26.8, 26.8, 29.1, 30.4, 32.8, 32.9, 33.4, 37.9, 55.3, 106.9, 112.8, 113.8, 127.1, 129.7, 132.8, 158.2, 199.7; 
HRMS (ESI) calcd for C$_{20}$H$_{28}$O [M+H]$^+$ m/z 285.2218, found 285.2214.

3n: yield 51%. According to General Procedure; colorless oil; Eluent: n-hexane/EtOAc = 200/1; 
$^1$H NMR (400 MHz CDCl$_3$, δ ppm): 1.14-1.21 (m, 3H), 1.31-1.41 (m, 3H), 1.69-1.79 (m, 3H), 1.86-1.97 (m, 4H), 2.09-2.21 (m, 3H), 2.34-2.40 (dt, $J_1 = 4.0$ Hz, $J_2 = 12.0$ Hz, 2H), 3.79 (s, 3H), 5.56 (s, 1H), 5.67 (s, 2H), 6.84-6.86 (d, $J = 8.0$ Hz, 2H), 7.30-7.32 (d, $J = 8.0$ Hz, 2H); 
$^{13}$C NMR (100 MHz CDCl$_3$, δ ppm): 25.1, 25.2, 25.8, 26.4, 26.7, 26.8, 29.1, 29.1, 31.3, 31.5, 32.8, 32.9, 33.3, 34.0, 37.8, 55.3, 100.3, 100.3, 112.6, 112.6, 113.8, 113.8, 126.3, 126.3, 126.8, 127.3, 129.5, 129.5, 158.2, 201.6, 201.7; 
HRMS (ESI) calcd for C$_{22}$H$_{28}$O [M+K]$^+$ m/z 347.1772, found 347.1761.
9. Characterization Data of Products 5a-5s, 3aa, 5ba, 6a-6c:

5a: yield 63%. According to General Procedure; colorless oil; Eluent: n-hexane/EtOAc = 300/1; 
$^1$H NMR (400 MHz CDCl$_3$, δ ppm): 1.10 (s, 9H), 1.15-1.25 (m, 3H), 1.32-1.41 (m, 2H), 1.69-1.80 (m, 3H), 1.85-1.93 (t, $J = 16.0$ Hz, 2H), 2.32 (s, 3H), 2.37-2.43 (dt, $J_1 = 4.0$ Hz, $J_2 = 12.0$ Hz, 1H), 5.48 (m, 1H), 7.09-7.11 (d, $J = 8.0$ Hz, 2H), 7.27-7.29 (d, $J = 8.0$ Hz, 2H); 
$^{13}$C NMR (100 MHz CDCl$_3$, δ ppm): 26.5, 26.8, 26.8, 29.1, 30.4, 32.4, 32.8, 33.4, 37.9, 55.3, 106.9, 112.8, 127.1, 129.7, 125.9, 128.4, 132.8, 158.2, 199.7; 
HRMS (ESI) calcd for C$_{20}$H$_{28}$ [M+H]$^+$ m/z 269.2269, found 269.2269.

5b: yield 47%. According to General Procedure; colorless oil; Eluent: n-hexane/EtOAc = 300/1; 
$^1$H NMR (400 MHz CDCl$_3$, δ ppm): 0.92-0.96 (t, $J = 8.0$ Hz, 3H), 1.11 (s, 9H), 1.15-1.21 (m, 3H), 1.31-1.41 (m, 2H), 1.60-1.65 (m, 2H), 1.70-1.79 (m, 3H), 1.80-1.94 (t, $J = 16.0$ Hz, 2H), 2.37-2.43 (dt, $J_1 = 4.0$ Hz, $J_2 = 12.0$ Hz, 1H), 2.53-2.57 (t, $J = 8.0$ Hz, 2H), 5.49 (m, 1H), 7.10-7.12 (d, $J = 8.0$ Hz, 2H), 7.29-7.31 (d, $J = 8.0$ Hz, 2H); 
$^{13}$C NMR (100 MHz CDCl$_3$, δ ppm): 13.9, 24.5, 26.5, 26.8, 26.9, 30.4, 32.8, 33.2, 33.4, 37.7, 37.8, 106.9, 113.2, 125.9, 128.4, 134.6, 140.7, 200.0; 
HRMS (ESI) calcd for C$_{24}$H$_{36}$ [M+H]$^+$ m/z 297.2577, found 297.2571.

5c: yield 51%. According to General Procedure; colorless oil; Eluent: n-hexane/EtOAc = 300/1; 
$^1$H NMR (400 MHz CDCl$_3$, δ ppm): 0.87-0.91 (t, $J = 8.0$ Hz, 3H), 1.11 (s, 9H), 1.15-1.21 (m, 3H), 1.32-1.38 (m, 6H), 1.58-1.61 (m, 2H), 1.69-1.79 (m, 3H), 1.88-1.94 (t, $J = 16.0$ Hz, 2H), 2.37-2.44 (dt, $J_1 = 4.0$ Hz, $J_2 = 12.0$ Hz, 1H), 2.55-2.58 (t, $J = 8.0$ Hz, 2H), 5.49 (m, 1H), 7.09-7.11 (d, $J = 8.0$ Hz, 2H), 7.29-7.31 (d, $J = 8.0$ Hz, 2H); 
$^{13}$C NMR (100 MHz CDCl$_3$, δ ppm): 14.0, 22.6, 26.5, 26.8, 26.9, 30.3, 30.4, 31.1, 31.5, 32.8, 32.9, 33.4, 35.5, 37.8, 106.9, 113.2, 125.9, 126.3, 128.3, 128.6, 134.6, 140.9, 200.0; 
HRMS (ESI) calcd for C$_{24}$H$_{36}$ [M+K]$^+$ m/z 363.2449, found 363.2441.
5d: yield 71%. According to General Procedure; colorless oil; Eluent: n-hexane/EtOAc = 100/1; 1H NMR (400 MHz CDCl3, δ ppm): 1.11 (s, 9H), 1.15-1.22 (m, 3H), 1.26-1.40 (m, 11H), 1.70-1.77 (m, 3H), 1.87-1.95 (t, J = 16.0 Hz, 2H), 2.38-2.44 (dt, J1 = 4.0 Hz, J2 = 12.0 Hz, 1H), 5.48-5.49 (t, J = 4.0 Hz, 1H), 7.33 (s, 4H); 13C NMR (100 MHz, CDCl3, δ ppm): 14.0, 22.6, 26.5, 26.8, 26.9, 30.3, 30.4, 31.1, 31.5, 32.8, 32.9, 33.4, 35.5, 37.8, 106.9, 113.2, 125.9, 126.3, 128.3, 128.6, 134.6, 140.9, 200.0; HRMS (ESI) calcd for C23H34 [M+K]+ m/z 349.2298, found 349.2292.

5e: yield 61%. According to General Procedure; colorless oil; Eluent: n-hexane/EtOAc = 200/1; 1H NMR (400 MHz CDCl3, δ ppm): 1.10 (s, 9H), 1.14-1.25 (m, 3H), 1.30-1.42 (m, 5H), 1.69-1.79 (m, 3H), 1.85-1.93 (t, J = 16.0 Hz, 2H), 2.34-2.40 (dt, J1 = 4.0 Hz, J2 = 12.0 Hz, 1H), 3.99-4.04 (dd, J1 = 8.0 Hz, J2 = 12.0 Hz, 2H), 5.48 (m, 1H), 6.82-6.84 (d, J = 8.0 Hz, 2H), 7.29-7.31 (d, J = 8.0 Hz, 2H); 13C NMR (100 MHz, CDCl3, δ ppm): 14.9, 14.9, 26.5, 26.8, 26.9, 30.4, 32.8, 32.9, 33.4, 35.5, 37.8, 106.8, 112.8, 114.4, 127.1, 129.5, 157.5, 199.6; HRMS (ESI) calcd for C21H30O [M+H]+ m/z 299.2375, found 299.2373.

5f: yield 83%. According to General Procedure; colorless oil; Eluent: n-hexane/EtOAc = 300/1; 1H NMR (400 MHz CDCl3, δ ppm): 1.13 (s, 9H), 1.17-1.28 (m, 3H), 1.34-1.44 (m, 2H), 1.71-1.82 (m, 3H), 1.90-1.98 (t, J = 16.0 Hz, 2H), 2.43-2.49 (dt, J1 = 4.0 Hz, J2 = 12.0 Hz, 1H), 5.54 (m, 1H), 7.29-7.33 (t, J = 8.0 Hz, 1H), 7.40-7.43 (t, J = 8.0 Hz, 2H), 7.46-7.48 (d, J = 8.0 Hz, 2H), 7.52-7.55 (d, J = 12.0 Hz, 2H), 7.57-7.59 (d, J = 12.0 Hz, 2H); 13C NMR (100 MHz, CDCl3, δ ppm): 26.5, 26.8, 26.9, 30.4, 32.9, 32.9, 33.4, 37.7, 107.1, 113.1, 126.5, 126.9, 127.0, 127.0, 128.7, 136.4, 139.0, 140.9, 200.5; HRMS (ESI) calcd for C23H30 [M+H]+ m/z 331.2426, found 331.2425.
5g: yield 53%. According to **General Procedure**: colorless oil; Eluent: *n*-hexane/EtOAc = 200/1; 

**$^1$H NMR** (400 MHz CDCl$_3$, δ ppm): 1.10 (s, 9H), 1.15-1.25 (m, 3H), 1.31-1.40 (m, 2H), 1.70-1.91 (m, 5H), 2.34-2.40 (dt, $J_1 = 8.0$ Hz, $J_2 = 12.0$ Hz, 1H), 5.50 (m, 1H), 6.96-6.70 (dt, $J_1 = 4.0$ Hz, $J_2 = 8.0$ Hz, 2H), 7.32-7.36 (dt, $J_1 = 4.0$ Hz, $J_2 = 8.0$ Hz, 2H); 

**$^{13}$C NMR** (100 MHz CDCl$_3$, δ ppm): 26.4, 26.7, 26.8, 30.4, 32.8, 32.8, 33.3, 38.0, 107.1, 112.5, 115.0-115.2 (d, $J = 21.0$ Hz), 127.5-127.6 (d, $J = 8.0$ Hz), 133.3 (d, $J = 3.0$ Hz), 160.3, 162.7, 200.0-200.1 (d, $J = 2.0$ Hz); 

**$^{19}$F NMR** (376 MHz CDCl$_3$, δ ppm): -117.0 (s, 1F); 

HRMS (ESI) calcd for C$_{19}$H$_{25}$F [M+K]$^+$ m/z 311.1577, found 311.1576.

5h: yield 60%. According to **General Procedure**: colorless oil; Eluent: *n*-hexane/EtOAc = 200/1; 

**$^1$H NMR** (400 MHz CDCl$_3$, δ ppm): 1.10 (s, 9H), 1.15-1.25 (m, 3H), 1.31-1.38 (m, 2H), 1.70-1.91 (m, 5H), 2.33-2.40 (dt, $J_1 = 4.0$ Hz, $J_2 = 12.0$ Hz, 1H), 5.51 (d, 1H), 7.24-7.26 (d, $J = 8.0$ Hz, 2H), 7.30-7.32 (d, $J = 8.0$ Hz, 2H); 

**$^{13}$C NMR** (100 MHz CDCl$_3$, δ ppm): 26.4, 26.7, 26.8, 30.4, 32.8, 32.8, 33.3, 37.7, 107.3, 112.6, 127.4, 128.4, 131.8, 135.9, 200.3; 

HRMS (ESI) calcd for C$_{19}$H$_{25}$Cl [M+H]$^+$ m/z 289.1723, found 289.1718.

5i: yield 55%. According to **General Procedure**: colorless oil; Eluent: *n*-hexane/EtOAc = 100/1; 

**$^1$H NMR** (400 MHz CDCl$_3$, δ ppm): 1.10 (s, 9H), 1.15-1.25 (m, 3H), 1.31-1.40 (m, 2H), 1.70-1.91 (m, 5H), 2.34-2.40 (dt, $J_1 = 8.0$ Hz, $J_2 = 12.0$ Hz, 1H), 5.50 (m, 1H), 6.96-6.70 (dt, $J_1 = 4.0$ Hz, $J_2 = 8.0$ Hz, 2H), 7.32-7.36 (dt, $J_1 = 4.0$ Hz, $J_2 = 8.0$ Hz, 2H); 

**$^{13}$C NMR** (100 MHz CDCl$_3$, δ ppm): 26.4, 26.7, 26.8, 30.3, 32.8, 33.3, 37.7, 107.4, 112.7 (d, $J = 2.0$ Hz), 112.8-113.0 (d, $J = 2.0$ Hz), 121.6 (d, $J = 3.0$ Hz), 129.5-129.6 (d, $J = 8.0$ Hz), 140.0-140.1 (d, $J = 7.0$ Hz), 161.9, 164.3, 200.5; 

**$^{19}$F NMR** (376 MHz CDCl$_3$, δ ppm): -113.9 (s, 1F); 

5j: yield 57%. According to **General Procedure**: colorless oil; Eluent: n-hexane/EtOAc = 200/1;

\(^1\)H NMR (400 MHz CDCl\(_3\), \(\delta\) ppm): 1.11 (s, 9H), 1.13-1.25 (m, 3H), 1.32-1.42 (m, 2H), 1.70-1.91 (m, 5H), 2.33-2.40 (dt, \(J_1 = 4.0\) Hz, \(J_2 = 12.0\) Hz, 1H), 5.53 (m, 1H), 7.12-7.14 (d, \(J = 8.0\) Hz, 1H), 7.19-7.23 (t, \(J = 8.0\) Hz, 1H), 7.25-7.34 (d, \(J = 8.0\) Hz, 1H), 5.53 (m, 1H);

\(^13\)C NMR (100 MHz CDCl\(_3\), \(\delta\) ppm): 22.6, 22.7, 26.4, 26.7, 26.8, 26.8, 28.6, 32.8, 33.2, 37.9, 102.6, 112.2, 115.0-115.2 (d, \(J = 11.0\) Hz), 127.6-127.7 (d, \(J = 8.0\) Hz), 133.3-133.4 (d, \(J = 3.0\) Hz), 160.3, 162.7, 201.4 (d, \(J = 1.0\) Hz);

\(^19\)F NMR (376 MHz CDCl\(_3\), \(\delta\) ppm): -117.0 (s, 1F);

HRMS (ESI) calcd for C\(_{19}\)H\(_{25}\)Cl [M+H]\(^+\) m/z 289.1723, found 289.1718.

5k: yield 50%. According to **General Procedure**: colorless oil; Eluent: n-hexane/EtOAc = 200/1;

\(^1\)H NMR (400 MHz CDCl\(_3\), \(\delta\) ppm): 1.06-1.08 (d, \(J = 8.0\) Hz, 6H), 1.13-1.25 (m, 4H), 1.30-1.41 (m, 3H), 1.70-1.90 (m, 5H), 2.33-2.44 (m, 2H), 5.52-5.53 (d, \(J = 4.0\) Hz, 1H), 6.96-6.70 (t, \(J = 8.0\) Hz, 2H), 7.31-7.35 (d, \(J_1 = 4.0\) Hz, \(J_2 = 12.0\) Hz, 2H);

\(^13\)C NMR (100 MHz CDCl\(_3\), \(\delta\) ppm): 25.6, 25.7, 26.4, 26.7, 26.8, 32.8, 33.2, 37.9, 102.6, 112.2, 115.0-115.2 (d, \(J = 11.0\) Hz), 127.6-127.7 (d, \(J = 8.0\) Hz), 133.3-133.4 (d, \(J = 3.0\) Hz), 160.3, 162.7, 201.4 (d, \(J = 1.0\) Hz);

\(^19\)F NMR (376 MHz CDCl\(_3\), \(\delta\) ppm): -117.0 (s, 1F);

HRMS (ESI) calcd for C\(_{18}\)H\(_{23}\)F [M+H]\(^+\) m/z 259.1857, found 259.1844.

5l: yield 35%. According to **General Procedure**: colorless oil; Eluent: n-hexane/EtOAc = 200/1;

\(^1\)H NMR (400 MHz CDCl\(_3\), \(\delta\) ppm): 0.92-0.97 (m, 6H), 1.16-1.25 (m, 4H), 1.31-1.37 (m, 3H), 1.53-1.67 (m, 10H), 1.75-1.79 (d, \(J = 16.0\) Hz, 2H), 1.87-2.02 (m, 5H), 2.08-2.17 (m, 1H), 2.36-2.42 (dt, \(J_1 = 4.0\) Hz, \(J_2 = 12.0\) Hz, 1H), 2.53-2.57 (t, \(J = 8.0\) Hz, 2H), 5.05-5.11 (m, 1H), 5.41-5.45 (t, \(J = 8.0\) Hz, 1H), 7.09-7.11 (d, \(J = 8.0\) Hz, 2H), 7.27-7.29 (d, \(J = 8.0\) Hz, 2H);

\(^13\)C NMR (100 MHz CDCl\(_3\), \(\delta\) ppm): 13.9, 17.6, 17.6, 19.7, 24.5, 25.6, 25.7, 26.5, 26.8, 26.8, 32.9, 33.1, 33.1, 33.2, 33.2, 33.3, 36.7, 36.7, 36.9, 37.7, 37.9, 93.4, 111.1, 124.8, 126.2, 128.4, 131.1, 131.1, 134.6, 140.6, 203.7, 203.7;

HRMS (ESI) calcd for C\(_{27}\)H\(_{40}\) [M+H]\(^+\) m/z 365.3203, found 365.3195.
**5m**: yield 47%. According to **General Procedure**; colorless oil; Eluent: n-hexane/EtOAc = 200/1;

**H NMR** (400 MHz CDCl₃, δ ppm): 1.10-1.12 (d, J = 8.0 Hz, 6H), 1.39-1.42 (t, J = 8.0 Hz, 3H), 1.44-1.50 (m, 1H), 1.87-1.99 (m, 2H), 2.09-2.10 (m, 2H), 2.17-2.21 (m, 1H), 2.34-2.40 (m, 1H), 2.73-2.80 (m, 1H), 4.00-4.05 (q, J = 8.0 Hz, 2H), 5.59 (s, 1H), 5.67 (s, 2H), 6.83-6.85 (d, J = 8.0 Hz, 2H), 7.30-7.32 (d, J = 8.0 Hz, 2H);

**C NMR** (100 MHz, CDCl₃, δ ppm): 14.9, 22.2, 22.2, 22.7, 25.0, 25.2, 27.8, 29.1, 29.1, 31.3, 31.5, 34.0, 34.0, 63.4, 100.6, 100.7, 113.6, 114.4, 126.3, 126.4, 126.8, 126.9, 127.3, 127.3, 127.4, 129.4, 129.4, 157.6, 201.1, 201.1;

**HRMS** (ESI) calcd for C₂₀H₂₆O [M+H]+ m/z 283.20 203.20

**5n**: yield 55%. According to **General Procedure**; colorless oil; Eluent: n-hexane/EtOAc = 200/1;

**H NMR** (400 MHz CDCl₃, δ ppm): 0.89-0.92 (dt, J₁ = 4.0 Hz, J₂ = 8.0 Hz, 3H), 1.08-1.12 (dt, J₁ = 4.0 Hz, J₂ = 8.0 Hz, 3H), 1.32-1.49 (m, 5H), 1.57-1.64 (m, 1H), 1.87-2.00 (m, 2H), 2.09-2.10 (m, 2H), 2.17-2.22 (m, 1H), 2.36-2.38 (m, 1H), 2.50-2.56 (m, 1H), 3.99-4.04 (q, J = 8.0 Hz, 2H), 5.57 (s, 1H), 5.67 (s, 2H), 6.83-6.85 (d, J = 8.0 Hz, 2H), 7.29-7.32 (dd, J₁ = 4.0 Hz, J₂ = 8.0 Hz, 2H);

**C NMR** (100 MHz, CDCl₃, δ ppm): 11.7, 11.7, 14.9, 25.0, 25.1, 26.2, 26.2, 27.2, 29.3, 29.3, 31.6, 31.7, 34.2, 42.2, 63.4, 100.2, 100.3, 110.5, 110.5, 114.3, 114.3, 126.3, 126.3, 126.9,

**5o**: yield 27%. According to **General Procedure**; colorless oil; Eluent: n-hexane/EtOAc = 200/1;

**H NMR** (400 MHz CDCl₃, δ ppm): 0.86-0.91 (m, 6H), 1.38-1.42 (t, J = 8.0 Hz, 3H), 1.45-1.53 (m, 5H), 1.87-2.00 (m, 2H), 2.10 (m, 2H), 2.18-2.22 (m, 1H), 2.33-2.38 (m, 2H), 3.99-4.05 (q, J = 8.0 Hz, 2H), 5.53-5.56 (t, J = 8.0 Hz, 1H), 5.68 (s, 2H), 6.82-6.84 (d, J = 8.0 Hz, 2H), 7.30-7.32 (d, J = 8.0 Hz, 2H);

**C NMR** (100 MHz, CDCl₃, δ ppm): 11.7, 11.7, 14.9, 25.0, 25.1, 26.2, 26.2, 27.2, 29.3, 29.3, 31.6, 31.7, 34.2, 42.2, 63.4, 100.2, 100.3, 110.5, 110.5, 114.3, 114.3, 126.3, 126.3, 126.9,
127.4, 130.5, 130.5, 157.6, 201.9, 201.9; 

**HRMS** (ESI) calcd for C_{22}H_{30}O [M+K]^+ m/z 349.1928, found 349.1926.

5p: yield 50%. According to **General Procedure**: colorless oil; Eluent: n-hexane/EtOAc = 200/1; 

**^1H NMR** (400 MHz CDCl₃, δ ppm): 0.85-0.87 (t, J = 4.0 Hz, 3H), 1.09-1.10 (t, J = 4.0 Hz, 3H), 1.26-1.31 (m, 8H), 1.38-1.42 (t, J = 8.0 Hz, 3H), 1.44-1.49 (m, 1H), 1.87-1.99 (m, 2H), 2.10 (m, 2H), 2.17-2.22 (m, 1H), 2.36-2.38 (d, J = 8.0 Hz, 1H), 2.57-2.59 (t, J = 4.0 Hz, 1H), 4.00-4.05 (q, J = 8.0 Hz, 2H), 5.57 (s, 1H), 5.67 (s, 2H), 6.83-6.85 (d, J = 8.0 Hz, 2H), 7.29-7.31 (d, J = 8.0 Hz, 2H);

**^13C NMR** (100 MHz CDCl₃, δ ppm): 14.1, 14.9, 19.8, 19.9, 20.8, 20.8, 22.7, 22.7, 25.0, 25.1, 25.2, 27.1, 27.2, 27.2, 29.1, 29.1, 29.2, 29.2, 31.3, 31.4, 31.5, 31.7, 32.1, 32.1, 33.1, 33.2, 33.2, 34.0, 34.0, 34.1, 34.2, 36.1, 36.1, 36.7, 36.7, 63.4, 76.7, 77.0, 77.3, 100.5, 100.6, 100.6, 112.7, 112.8, 114.4, 126.2, 126.3, 126.8, 127.3, 129.7, 129.8, 158.6, 201.4, 201.5, 201.5.

**HRMS** (ESI) calcd for C_{24}H_{34}O [M+K]^+ m/z 377.2247, found 377.2248.

5q: yield 43%. According to **General Procedure**: colorless oil; Eluent: n-hexane/EtOAc = 200/1; 

**^1H NMR** (400 MHz CDCl₃, δ ppm): 1.38-1.42 (t, J = 8.0 Hz, 3H), 1.44-1.52 (m, 3H), 1.58-1.68 (m, 4H), 1.87-1.95 (m, 4H), 2.09-2.10 (t, J = 4.0 Hz, 2H), 2.17-2.21 (d, J = 16.0 Hz, 1H), 2.35-2.41 (m, 1H), 2.88-2.92 (m, 1H), 4.00-4.05 (q, J = 8.0 Hz, 2H), 5.55-5.58 (t, J = 8.0 Hz, 1H), 5.67 (s, 2H), 6.83-6.84 (d, J = 4.0 Hz, 2H), 7.33-7.35 (d, J = 8.0 Hz, 2H);

**^13C NMR** (100 MHz CDCl₃, δ ppm): 14.9, 25.1, 25.1, 25.2, 29.1, 31.2, 31.5, 32.3, 32.4, 32.9, 34.1, 39.3, 63.4, 100.5, 100.6, 111.5, 114.3, 126.2, 126.3, 126.9, 127.4, 157.6, 200.8, 200.8.

**HRMS** (ESI) calcd for C_{22}H_{28}O [M+K]^+ m/z 347.1777, found 347.1775.

5s: yield 57%. According to **General Procedure**: colorless oil; Eluent: n-hexane/EtOAc = 200/1; 

**^1H NMR** (400 MHz CDCl₃, δ ppm): 0.88-0.91 (t, J = 6.0 Hz, 3H) 1.01-1.07 (t, J = 12.0 Hz, 2H), 1.10-1.26 (m, 4H), 1.38-1.43 (m, 2H), 1.62-1.73 (m, 6H), 1.88-1.93 (m, 2H), 3.31-3.32 (d, J = 4.0 Hz, 2H), 5.25-5.26 (d, J = 4.0 Hz 1H), 6.17-6.21 (m, 2H), 7.23-7.30 (m, 3H);
**13C NMR** (100 MHz, CDCl₃, δ ppm): 14.0, 21.1, 26.4, 26.6, 32.3, 32.4, 33.1, 36.6, 40.8, 76.7, 77.0, 77.3, 92.1, 110.3, 125.9, 128.2, 128.5, 128.6, 141.2, 201.0.

**HRMS** (ESI) calcd for C₃₉H₃₆ [M+Na]+ m/z 277.1932, found 277.1930.

3aa: yield 17%. According to **General Procedure**; colorless oil; Eluent: n-hexane/EtOAc = 200/1;

**1H NMR** (400 MHz CDCl₃, δ ppm): 0.50-0.56 (m, 1H), 0.60-0.75 (m, 4H), 0.90-1.28 (m, 10H), 1.43-1.46 (d, J = 12.0 Hz, 2H), 1.52-1.55 (d, J = 12.0 Hz, 2H), 1.61-1.64 (d, J = 12.0 Hz, 2H), 2.76-2.81 (t, J = 12.0 Hz, 1H), 5.27 (s, 2H), 7.12-7.16 (t, J = 8.0 Hz, 1H), 7.30-7.43 (m, 10H), 7.60-7.62 (d, J = 8.0 Hz, 4H);

**13C NMR** (100 MHz, CDCl₃, δ ppm): 25.4, 26.6, 26.9, 28.6, 33.2, 46.9, 50.2, 62.7, 115.8, 125.0, 126.9, 127.6, 127.8, 127.9, 141.0, 145.2, 151.2;

**HRMS** (ESI) calcd for C₃₅H₃₉N [M+H]+ m/z 474.3161, found 474.3156.

5ba: yield 17%. According to **General Procedure**; colorless oil; Eluent: n-hexane/EtOAc = 200/1;

**1H NMR** (400 MHz CDCl₃, δ ppm): 0.90-0.94 (t, J = 8.0 Hz, 3H), 1.05 (s, 9H), 1.59-1.66 (m, 2H), 2.26 (s, 2H), 2.54-2.58 (t, J = 8.0 Hz, 2H), 7.08-7.10 (d, J = 8.0 Hz, 2H), 7.31-7.33 (d, J = 8.0 Hz, 2H);

**13C NMR** (100 MHz, CDCl₃, δ ppm): 13.7, 24.4, 29.1, 31.4, 34.5, 37.9, 82.1, 88.0, 121.4, 128.3, 131.4, 142.2;

**HRMS** (ESI) calcd for C₁₆H₂₂ [M+H]+ m/z 215.1800, found 215.1798.

6a: yield 12%. According to **General Procedure**; colorless oil; Eluent: n-hexane/EtOAc = 200/1;

**1H NMR** (400 MHz CDCl₃, δ ppm): 1.11-1.21 (m, 9H), 1.26-1.54 (m, 12H), 1.76-2.04 (m, 2H), 2.12-2.24 (m, 5H), 3.99-4.04 (q, J = 8.0 Hz, 2H), 4.62-4.64 (t, J = 4.0 Hz, 1H), 5.66-5.75 (m, 2H), 6.79-6.81 (d, J = 8.0 Hz, 2H), 7.32-7.34 (d, J = 8.0 Hz, 2H);

**13C NMR** (100 MHz, CDCl₃, δ ppm): 14.7, 17.2, 20.4, 24.0, 25.1, 25.3, 25.5, 26.8, 28.1, 33.9, 34.6, 38.7, 38.9, 40.2, 59.5, 60.5, 63.4, 78.7, 79.4, 86.6, 86.8, 88.0, 88.1, 114.3, 115.7, 126.3, 126.5, 126.7, 127.0, 132.7, 158.6;

**HRMS** (ESI) calcd for C₂₆H₃₇NO₂ [M+H]+ m/z 396.2903, found 396.2899.
6b + 6c: yield 23%. According to General Procedure; colorless oil; Eluent: n-hexane/EtOAc = 200/1;

\[ ^1H \text{NMR} \text{ (400 MHz CDCl}_3, \delta \text{ ppm):} \ 1.38-1.42 \text{ (t, J = 8.0 Hz, 3H), 1.86-2.38 (m, 8H), 3.99-4.04 (q, J = 8.0 Hz, 2H), 5.59-5.67 (m, 2.4H), 6.05-6.16 (m, 0.38H), 6.78-6.84 (m, 2H), 7.19-7.21 (d, J = 8.0 Hz, 0.76H), 7.30-7.33 (d, J = 12.0 Hz, 1.26H);} \]

\[ ^13C \text{NMR} \text{ (100 MHz CDCl}_3, \delta \text{ ppm):} \ 14.8, 14.8, 24.9, 25.0, 26.3, 28.2, 28.8, 28.9, 31.2, 31.3, 31.4, 33.4, 33.6, 33.7, 63.5, 63.5, 81.3, 87.1, 95.2, 95.2, 100.2, 100.2, 114.4, 114.7, 114.7, 116.1, 126.0, 126.1, 126.2, 126.6, 126.7, 126.8, 126.9, 127.2, 127.2, 127.5, 127.6, 132.8, 158.0, 158.4, 203.5, 203.6; \]

\[ \text{HRMS} \text{ (ESI) calcd for C}_{17}\text{H}_{20}\text{O }[\text{M+H}]^+ m/z 241.1592, \text{ found 241.1589}. \]
10. $^1$H NMR and $^{13}$C NMR Spectra of the Substrates 1a-1b, 4a-4l, 4s:
11. $^1H$ NMR and $^{13}C$ NMR Spectra of the Products 3a-3n:

3a, 79%  
d.r. = 1:1
OMe

3f, 45%
3k, 53% d.r. = 1:1
12. $^1$H NMR and $^{13}$C NMR Spectra of Products 5a-5s, 3aa, 5ba, 6a-6c:
5g, 53%
5h, 60%
5k, 50%
$\text{EtO}$

$5m, 47\%$

$d.r. = 1:1$
5ba, 17%
w/o 4A MS
23% yield, 6b : 6c = 5 : 3