Regio- and stereo-selective decarbonylative alkylative arylation of terminal alkynes with aliphatic aldehydes and arenes via dual C-H bond functionalization

Yong Peng, Feng Zhang, Ting-Ting Qin, Cong-Ling Xu and Luo Yang*

Table of Contents
I. General information ............................................................................................................. 1
II. General experimental procedure ......................................................................................... 2
III. Condition optimization ...................................................................................................... 2
  Table S1. Optimization of the catalysts .................................................................................. 2
  Table S2. Optimization of the temperature ........................................................................... 3
  Table S3. Optimization of the amounts of oxidants ............................................................... 3
  Table S4. Optimization of the amounts of catalyst ................................................................. 4
  Table S5. Optimization of the amounts of solvent ................................................................. 4
  Table S6. Optimization of the time ....................................................................................... 4
IV. KIE experiments ................................................................................................................. 5
V. DFT calculations .................................................................................................................. 6
VI. The assignment of the configuration by NOE ................................................................. 7
VII. Spectra data of products 4a-4i, 5b-5m, 6b-6m ............................................................... 9
VIII. References ....................................................................................................................... 20
IX. Copies of $^1$H and $^{13}$C NMR spectra of products 4a-4i, 5b-5m, 6b-6m ....................... 21

I. General information

Unless otherwise noted, all commercially available compounds were used as purchased without further purification. Dry solvents (toluene, ethyl acetate, dichloromethane, acetonitrile, chlorobenzene, fluorobenzene, trifluoromethyl benzene) were used as commercially available. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) or Sorbent Silica Gel 60 F254 plates. The developed chromatography was analyzed by UV lamp (254 nm). High-resolution mass spectra (HRMS) were obtained from a JEOL JMS-700 instrument (ESI). Melting points are uncorrected. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature. Chemical shifts for $^1$H NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard (chloroform: $\delta$ 7.26 ppm). Chemical shifts for $^{13}$C NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard (CDCl$_3$: $\delta$ 77.16 ppm). Data are reported as following: chemical shift, multiplicity (s =
singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet, br = broad signal), coupling constant (Hz), and integration.

The Z/E ratio was determined by GC of reaction mixtures by assuming the Z/E-isomers with the same responses under the FID detector. The ratio of regio-isomers for the products from mono-substituted arenes was determined by $^1$H NMR.

II. General experimental procedure

An oven-dried reaction vessel was successively charged with CuBr$_2$ (0.05 mmol, 25 mol%), benzene (3a, 4 mL), ethyl propiolate (2a, 0.2 mmol, 1.0 equiv), pivalaldehyde (1a, 0.6 mmol, 3 equiv) and di-tert-butyl peroxide (DTBP, 0.6 mmol, 3 equiv). The vessel was sealed and stirred at 110 °C (oil bath temperature) for 24 h. Afterwards the resulting mixture was cooled to room temperature, the solvent was removed in vacuum. The residue was purified by column chromatography on silica gel with a mixture of dichloromethane/petroleum ether (1:3) as eluent to give products 4a.

III. Condition optimization

<table>
<thead>
<tr>
<th>entry</th>
<th>Cat. (mol%)</th>
<th>Yield [%] $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>--</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>Fe(OAc)$_2$</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>Fe(acac)$_2$</td>
<td>7</td>
</tr>
<tr>
<td>4</td>
<td>FeCl$_2$</td>
<td>11</td>
</tr>
<tr>
<td>5</td>
<td>CoCl$_2$</td>
<td>12</td>
</tr>
<tr>
<td>6</td>
<td>Co(OAc)$_2$</td>
<td>8</td>
</tr>
<tr>
<td>7</td>
<td>Co(acac)$_2$</td>
<td>9</td>
</tr>
<tr>
<td>8</td>
<td>NiCl$_2$</td>
<td>8</td>
</tr>
<tr>
<td>9</td>
<td>Ni(acac)$_2$</td>
<td>8</td>
</tr>
<tr>
<td>10</td>
<td>Ni(OAc)$_2$</td>
<td>10</td>
</tr>
<tr>
<td>11</td>
<td>CuBr</td>
<td>20</td>
</tr>
<tr>
<td>12</td>
<td>Cu(OAc)$_2$</td>
<td>13</td>
</tr>
<tr>
<td>13</td>
<td>Cu(acac)$_2$</td>
<td>4</td>
</tr>
<tr>
<td>14</td>
<td>CuBr$_2$</td>
<td>25</td>
</tr>
<tr>
<td>15</td>
<td>Cu$_2$O</td>
<td>17</td>
</tr>
</tbody>
</table>
16 CuCl 19
17 CuF₂·2H₂O 14
18 CuCN 11
19 CuSO₄ 8

* Reaction conditions: 2a (0.2 mmol, 1.0 equiv), 1a (0.6 mmol, 3.0 equiv), 3a (1 mL), DTBP (0.6 mmol, 3.0 equiv), Cat. (0.01 mmol, 5 mol%), stirred at 120 °C for 24 h under air. * Isolated yields.

Table S2. Optimization of the temperature

<table>
<thead>
<tr>
<th>entry</th>
<th>Temp. (℃)</th>
<th>Yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>80</td>
<td>19</td>
</tr>
<tr>
<td>2</td>
<td>90</td>
<td>31</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>42</td>
</tr>
<tr>
<td>4</td>
<td>110</td>
<td>49</td>
</tr>
<tr>
<td>5</td>
<td>120</td>
<td>25</td>
</tr>
<tr>
<td>6</td>
<td>130</td>
<td>17</td>
</tr>
</tbody>
</table>

* Reaction conditions: 2a (0.2 mmol, 1.0 equiv), 1a (0.6 mmol, 3.0 equiv), 3a (1 mL), DTBP (0.6 mmol, 3.0 equiv), CuBr₂ (0.01 mmol, 5 mol%), for 24 h under air. * Isolated yields.

Table S3. Optimization of the amounts of oxidants

<table>
<thead>
<tr>
<th>entry</th>
<th>[O] (X equiv)</th>
<th>Yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TBHP in water</td>
<td>17</td>
</tr>
<tr>
<td>2</td>
<td>TBHP in decane</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>H₂O₂</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>DTBP (3 eq)</td>
<td>49</td>
</tr>
<tr>
<td>5</td>
<td>DTBP (2 eq)</td>
<td>28</td>
</tr>
<tr>
<td>6</td>
<td>DTBP (4 eq)</td>
<td>41</td>
</tr>
</tbody>
</table>

* Reaction conditions: 2a (0.2 mmol, 1.0 equiv), 1a (0.6 mmol, 3.0 equiv), 3a (1 mL), DTBP (X equiv), CuBr₂ (0.01 mmol, 5 mol%), stirred at 120 °C for 24 h under air. * Isolated yields.
Table S4. Optimization of the amounts of catalysts

![Chemical reaction diagram]

<table>
<thead>
<tr>
<th>entry</th>
<th>CuBr₂ (X %)</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>49</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>52</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>55</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>60</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>76</td>
</tr>
<tr>
<td>6</td>
<td>30</td>
<td>48</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: 2a (0.2 mmol, 1.0 equiv), 1a (0.6 mmol, 3.0 equiv), 3a (1 mL), DTBP (0.6 mmol, 3.0 equiv), CuBr₂ (X %), stirred at 120 °C for 24 h under air. <sup>b</sup> Isolated yields.

Table S5. Optimization of the amounts of solvent

![Chemical reaction diagram]

<table>
<thead>
<tr>
<th>entry</th>
<th>Sol (X mL)</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>76</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>78</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>83</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>88</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: 2a (0.2 mmol, 1.0 equiv), 1a (0.6 mmol, 3.0 equiv), 3a (X mL), DTBP (0.6 mmol, 3.0 equiv), CuBr₂ (25 %), stirred at 120 °C for 24 h under air. <sup>b</sup> Isolated yields.

Table S6. Optimization of the time

![Chemical reaction diagram]

<table>
<thead>
<tr>
<th>entry</th>
<th>h</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12</td>
<td>57</td>
</tr>
<tr>
<td>2</td>
<td>16</td>
<td>74</td>
</tr>
</tbody>
</table>
3 20 84
4 24 88

*Reaction conditions: 2a (0.2 mmol, 1.0 equiv), 1a (3 equiv), 3a (4 mL), DTBP (0.6 mmol, 3.0 equiv), CuBr2 (25 %), stirred at 120 °C under air. *Isolated yields.

IV. KIE experiments

(a) Synthesis of 2-phenylacetaldehyde-D1 (D1-1f)

(i) To a stirred suspension of LiAlD4 (0.23 g, 6 mmol) in dry THF (3 ml) was added dropwise a solution of methyl methyl 2-phenylacetate (0.75 g, 5 mmol) in dry THF (10 ml) at 0 °C. After 1.5 h at room temperature, the reaction was quenched by addition with 40% KOH at 0 °C. The precipitate was filtered off and washed with ether. The combined filtrates were evaporated and the residue was purified by column chromatography on silica gel (hexane : ethyl acetate = 10 : 1) to give 2-phenylethan-1-ol-D2 (0.52 g, 85%) as a yellow oil.

(ii) Dess-Martin periodinane (2.12 g, 5 mmol) was added to a solution of above 2-phenylethan-1-ol-D2 (4.3 mmol) in 15 mL of CH2Cl2. The reaction mixture was stirred until the alcohol was no longer detectable (TLC). The mixture was suction filtered and concentrated under reduced pressure. The residue was further purified by column chromatography on silica gel to give 2-phenylacetaldehyde-D1 (D1-1f) (0.49 g, 95%) as a colorless oil.

(b) Competing experiments

a) ![Reaction scheme](image)

\[ KIE^1 = \frac{22}{16} = 1.4 \]

b) ![Reaction scheme](image)

\[ KIE^2 = \frac{8.7}{2.1} = 4.1 \]

*Two microwave reaction vessels was separately charged with charged with CuBr2 (0.025 mmol, 12.5 mmol%), benzene (3a, 2 mL), (or benzene D6-3a) ethyl propiolate (2a, 0.1 mmol, 1.0 equiv), pivalaldehyde (1a, 0.3 mmol, 1.5 equiv) and di-tert-butyl peroxide (DTBP, 0.3 mmol, 1.5 equiv). The vessel was sealed and stirred at 110 °C (oil bath temperature) for 1 h. Yield of 4a and 4a-D5 was detected by GC.

b) Two microwave reaction vessels was separately charged with charged with CuBr2 (0.025 mmol, 12.5 mol%), benzene (3a, 2 mL), ethyl propiolate (2a, 0.1 mmol, 1.0 equiv), 2-phenylacetaldehyde (1f, 0.3 mmol, 1.5 equiv) (or 2-phenylacetaldehyde D1-1f) and di-tert-butyl peroxide (DTBP, 0.3 mmol, 1.5 equiv). The vessel was sealed and stirred at 110 °C (oil bath temperature) for 1 h. Yield
of 5f was detected by GC.

\[ \text{6 mol\% CuBr}_2 \text{ benzene} \]

\[ \begin{align*}
\text{CO}_2\text{Et} & \quad \text{110 °C, 12 h} \\
5k-Z & \quad 5k-Z + 5k-E \\
\text{with CuBr}_2: Z:E = 2.5:1 \\
\text{without CuBr}_2: Z:E = 7:1
\end{align*} \]

A microwave reaction vessels was separately charged with charged with CuBr$_2$ (0.006 mmol, 6 mmol%), benzene (3a, 1 mL) and ethyl (Z)-4-methyl-2-phenylpent-2-enoate (5k-Z, 0.05 mmol). The vessel was sealed and stirred at 110 °C (oil bath temperature) for 12 h. Yield of 5k-Z and 5k-E was detected by GC.

A microwave reaction vessels was separately charged with benzene (3a, 1 mL) and ethyl (Z)-4-methyl-2-phenylpent-2-enoate (5k-Z, 0.05 mmol). The vessel was sealed and stirred at 110 °C (oil bath temperature) for 12 h. Yield of 5k-Z and 5k-E was detected by GC.

V. DFT calculations

Computational Details

All DFT calculations were carried out with Gaussian03 quantum chemical package. The geometry optimizations were performed with B3LYP functional and the 6-311+G(d) basis set. For those structures having various conformations, the most stable conformer was searched and utilized. Vibrational frequency calculations were carried out at the same level of theory as the geometry optimizations. Free energy changes were calculated based on the optimized gas phase structures.

The calculation out-put files and coordinates were included in the separated zipped file.

References

Gaussian 03, Revision B.05,
M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria,
M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven,
K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi,
V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega,
G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota,
R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao,
H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross,
C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev,
A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala,
K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg,
V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain,
O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavanchary,
J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford,
J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz,
I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham,
C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill,
B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople,
VI. The assignment of the configuration by NOE

(a) ethyl (Z)-4,4-dimethyl-2-phenylpent-2-enoate (4a)
(b) ethyl (Z)-2-mesityl-4,4-dimethylpent-2-enoate (6g)
VII Spectra data of products 4a-4i, 5b-5m, 6b-6m

(4a) ethyl \((Z)\)-4,4-dimethyl-2-phenylpent-2-enoate

![Chemical structure of 4a]

The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (2a) with pivalaldehyde (1a) and benzene (3a), and purified by flash column chromatography as colorless oil (40.8 mg, 88%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.34 – 7.25 (m, 5H), 5.90 (s, 1H), 4.27 (q, \(J = 7.2\) Hz, 2H), 1.32 (t, \(J = 7.2\) Hz, 3H), 1.18 (s, 9H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 170.02, 142.45, 138.08, 132.29, 128.57, 127.68, 126.09, 61.05, 33.98, 29.86, 14.15. IR (cm\(^{-1}\)): 3083, 3059, 2905, 2870, 1727, 1540, 751.

(4b) benzyl \((Z)\)-4,4-dimethyl-2-phenylpent-2-enoate

![Chemical structure of 4b]

The title compound was prepared according to the general procedure described above by the reaction between benzyl propiolate (2b) with pivalaldehyde (1a) and benzene (3a), and purified by flash column chromatography as yellow oil (50.6 mg, 86%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.36 – 7.31 (m, 5H), 7.29 – 7.25 (m, 5H), 5.92 (s, 1H), 5.25 (s, 2H), 1.15 (s, 9H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 169.85, 142.94, 137.93, 135.37, 131.88, 128.78, 128.64, 128.60, 128.46, 127.75, 126.18, 67.06, 34.05, 29.88. IR (cm\(^{-1}\)): 3096, 3054, 2936, 2867, 1776, 1540, 694. HRMS: calcd. for C\(_{20}\)H\(_{22}\)NaO\(_2\)^+ [M+Na]^+: 317.1512; Found: 317.1497.

(4c) phenyl \((Z)\)-4,4-dimethyl-2-phenylpent-2-enoate

![Chemical structure of 4c]

The title compound was prepared according to the general procedure described above by the reaction between phenyl propiolate (2c) with pivalaldehyde (1a) and benzene (3a), and purified by flash column chromatography as yellow oil (60 mg, 91%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.46 – 7.30 (m, 8H), 7.16 (d, \(J = 8.0\) Hz, 2H), 6.05 (s, 1H), 1.29 (s, 9H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 168.17, 150.69, 144.12, 137.91, 131.65, 129.66, 128.82, 128.00, 126.36, 126.17, 121.52, 34.33, 30.06. IR (cm\(^{-1}\)): 3089, 3066, 2954, 2843, 1647, 1558, 747. HRMS: calcd. for C\(_{19}\)H\(_{20}\)NaO\(_2\)^+ [M+Na]^+: 303.1356; Found: 303.1337

(4d) naphthalen-2-yl \((Z)\)-4,4-dimethyl-2-phenylpent-2-enoate

![Chemical structure of 4d]
The title compound was prepared according to the general procedure described above by the reaction between naphthalen-2-yl propiolate (2d) with pivalaldehyde (1a) and benzene (3a), and purified by flash column chromatography as yellow oil (52.8 mg, 80%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.89 – 7.80 (m, 5H), 7.49 (d, $J$ = 8.0 Hz, 4H), 7.41 (t, $J$ = 8.0 Hz, 2H), 7.30 (dd, $J$ = 8.0, 1.8 Hz, 1H), 6.08 (s, 1H), 1.33 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.31, 159.20, 148.33, 144.29, 137.94, 133.88, 131.67, 131.59, 130.35, 129.64, 128.87, 128.57, 128.05, 127.92, 127.83, 126.75, 126.41, 125.94, 124.70, 122.00, 118.49, 34.38, 30.10. IR (cm$^{-1}$): 3362, 3209, 2937, 2844, 1646, 1570, 745.

Mass spectrum: calcd. for C$_{19}$H$_{20}$Na$_2$O$_2$ $^+$$[M+Na]^+$: 353.1512; Found: 353.1517.

(4e) (Z)-4,4-dimethyl-N,2-diphenylpent-2-enamide

The title compound was prepared according to the general procedure described above by the reaction between N-phenyl-O-propioloxyhydroxylamine (2e) with pivalaldehyde (1a) and benzene (3a), and purified by flash column chromatography as yellow solid (45.2 mg, 81%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 – 7.55 (m, 2H), 7.46 – 7.44 (m, 2H), 7.36 – 7.28 (m, 5H), 7.26 (s, 1H), 7.14 (t, $J$ = 6.0 Hz, 1H), 6.00 (s, 1H), 1.25 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.11, 142.32, 138.06, 137.72, 135.34, 129.25, 128.84, 127.95, 126.10, 124.69, 119.87, 34.40, 30.20. IR (cm$^{-1}$): 3061, 3043, 2906, 2748, 1751, 1615, 748. Melting point: 158-162 °C.

(4f) (Z)-O-(4,4-dimethyl-2-phenylpent-2-enoyl)hydroxylamine

The title compound was prepared according to the general procedure described above by the reaction between propiolamide (2f) with pivalaldehyde (1a) and benzene (3a), and purified by flash column chromatography as yellow solid (21.9 mg, 50%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33 – 7.24 (m, 5H), 6.18 (s, 1H), 6.05 (s, 1H), 5.91 (s, 1H), 1.18 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 173.50, 142.47, 137.95, 132.10, 128.56, 127.67, 126.01, 33.94, 29.78. IR (cm$^{-1}$): 3297, 3060, 2958, 2870, 1727, 1635, 1478, 754. HRMS: calcd. for C$_{13}$H$_{17}$NNaO$^+$ [M+Na]$^+$: 226.1202; Found: 226.1229.

(4g) cinnamyl (Z)-4,4-dimethyl-2-phenylpent-2-enoate

The title compound was prepared according to the general procedure described above by the reaction between cinnamyl propiolate (2g) with pivalaldehyde (1a) and benzene (3a), and purified by flash column chromatography as yellow oil (38.2 mg, 67%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.49 – 7.41 (m, 5H), 7.41 – 7.35 (m, 4H), 7.35 – 7.24 (m, 5H), 7.24 – 7.17 (m, 5H), 7.17 – 7.10 (m, 5H), 6.08 (s, 1H), 1.33 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.31, 159.20, 148.33, 144.29, 137.94, 133.88, 131.67, 131.59, 130.35, 129.64, 128.87, 128.57, 128.05, 127.92, 127.83, 126.75, 126.41, 125.94, 124.70, 122.00, 118.49, 34.38, 30.10. IR (cm$^{-1}$): 3362, 3209, 2937, 2844, 1646, 1570, 745. HRMS: calcd. for C$_{19}$H$_{20}$Na$_2$O$_2$ $^+$$[M+Na]^+$: 353.1512; Found: 353.1517.

(4h) (Z)-4,4-dimethyl-2-phenylpent-2-enoamide

The title compound was prepared according to the general procedure described above by the reaction between cinnamyl propiolamide (2h) with pivalaldehyde (1a) and benzene (3a), and purified by flash column chromatography as yellow solid (35.9 mg, 60%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.49 – 7.41 (m, 5H), 7.41 – 7.35 (m, 4H), 7.35 – 7.24 (m, 5H), 7.24 – 7.17 (m, 5H), 7.17 – 7.10 (m, 5H), 6.08 (s, 1H), 1.33 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.31, 159.20, 148.33, 144.29, 137.94, 133.88, 131.67, 131.59, 130.35, 129.64, 128.87, 128.57, 128.05, 127.92, 127.83, 126.75, 126.41, 125.94, 124.70, 122.00, 118.49, 34.38, 30.10. IR (cm$^{-1}$): 3362, 3209, 2937, 2844, 1646, 1570, 745. HRMS: calcd. for C$_{19}$H$_{20}$Na$_2$O$_2$ $^+$$[M+Na]^+$: 353.1512; Found: 353.1517.
The title compound was prepared according to the general procedure described above by the reaction between cinnamyl propiolate (2g) with pivalaldehyde (1a) and benzene (3a), and purified by flash column chromatography as yellow oil (33.3 mg, 52%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 (t, $J = 6.4$ Hz, 5H), 7.33 (t, $J = 7.2$ Hz, 5H), 6.70 (d, $J = 15.6$ Hz, 1H), 6.30 – 6.26 (m, 1H), 5.93 (s, 1H), 4.85 (t, $J = 6.4$ Hz, 2H), 1.23 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.92, 152.65, 143.79, 137.92, 135.98, 135.73, 128.79, 128.67, 128.49, 127.89, 126.86, 126.48, 121.74, 66.91, 34.05, 29.86. IR (cm$^{-1}$): 3297, 3092, 2976, 2861, 1703, 1647, 755.

HRMS: calcd. for C$_{22}$H$_{24}$NaO$_2$ $^+ [M+Na]^+$: 343.1669; Found: 343.1670.

(4h) (Z)-4,4-dimethyl-2-phenylpent-2-en-1-yl acetate

The title compound was prepared according to the general procedure described above by the reaction between prop-2-yn-1-yl acetate (2h) with pivalaldehyde (1a) and benzene (3a), and purified by flash column chromatography as colorless oil (33.9 mg, 73%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33 – 7.24 (m, 5H), 5.98 (s, 1H), 5.10 (s, 2H), 2.00 (s, 3H), 1.23 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 171.28, 145.94, 142.58, 133.43, 128.36, 127.08, 126.56, 61.58, 33.56, 31.53, 21.15. IR (cm$^{-1}$): 3104, 3063, 2978, 2863, 1699, 1487, 756. HRMS: calcd. for C$_{14}$H$_{18}$Na$^+$ [M+Na]$^+$: 255.1356; Found: 255.1341.

(4i) (Z)-(1-cyclopropyl-3,3-dimethylbut-1-en-1-yl)benzene

The title compound was prepared according to the general procedure described above by the reaction between ethynylcyclopropane (2i) with pivalaldehyde (1a) and benzene (3a), and purified by flash column chromatography as yellow oil (24 mg, 60%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30 – 7.08 (m, 5H), 5.23 – 5.10 (m, 1H), 2.37 – 2.27 (m, 1H), 1.25 (s, 2H), 1.11 (s, 2H), 1.01 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.44, 137.87, 133.79, 128.42, 127.61, 127.07, 36.35, 30.22, 20.49, 14.41, 12.08. IR (cm$^{-1}$): 3185, 3073, 2988, 2813, 1699, 1487, 756. HRMS: calcd. for C$_{14}$H$_{18}$Na$^+$ [M+Na]$^+$: 208.1222; Found: 208.1230.

(5b) ethyl (Z)-4-methyl-2-phenylhex-2-enoate

The title compound was prepared according to the general procedure described above by the reaction between ethynylcyclopropane (2i) with pivalaldehyde (1a) and benzene (3a), and purified by flash column chromatography as yellow oil (24 mg, 60%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30 – 7.08 (m, 5H), 5.23 – 5.10 (m, 1H), 2.37 – 2.27 (m, 1H), 1.25 (s, 2H), 1.11 (s, 2H), 1.01 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.44, 137.87, 133.79, 128.42, 127.61, 127.07, 36.35, 30.22, 20.49, 14.41, 12.08. IR (cm$^{-1}$): 3185, 3073, 2988, 2813, 1699, 1487, 756. HRMS: calcd. for C$_{14}$H$_{18}$Na$^+$ [M+Na]$^+$: 208.1222; Found: 208.1230.
The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (2a) with 2-methylbutanal (1b) and benzene (3a), and purified by flash column chromatography as colorless oil (35.7 mg, 77%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33 – 7.27 (m, 5H), 5.91 (d, $J = 10.4$ Hz, 1H), 4.29 (q, $J = 7.2$ Hz, 2H), 2.75 – 2.64 (m, 1H), 1.49 – 1.37 (m, 2H), 1.32 (t, $J = 7.2$ Hz, 3H), 1.08 (d, $J = 6.4$ Hz, 3H), 0.92 (t, $J = 7.6$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.72, 144.44, 137.87, 133.79, 128.42, 127.61, 127.07, 77.48, 77.16, 76.84, 60.84, 36.35, 30.42, 20.49, 14.41, 12.08. IR (cm$^{-1}$): 3143, 3069, 2965, 2870, 1697, 1560, 755.

HRMS: calcd. for C$_{15}$H$_{20}$NaO$_2$ $^{[M+Na]^+}$: 255.1356; Found: 255.1347.

(5c) ethyl (Z)-4-ethyl-2-phenylhex-2-enoate

The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (2a) with 2-ethylbutanal (1c) and benzene (3a), and purified by flash column chromatography as colorless oil (38.4 mg, 78%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34 – 7.27 (m, 5H), 5.85 (d, $J = 10.4$ Hz, 1H), 4.29 (q, $J = 7.2$ Hz, 2H), 2.56 – 2.47 (m, 1H), 1.57 – 1.50(m, 3H), 1.32 (t, $J = 7.0$ Hz, 4H), 0.91 (t, $J = 7.6$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.82, 143.04, 137.95, 135.28, 128.44, 127.61, 127.02, 60.78, 43.36, 28.15, 14.42, 12.02. IR (cm$^{-1}$): 3179, 3086, 2929, 2874, 1722, 1643, 755. HRMS: calcd. for C$_{15}$H$_{19}$NaO$_2$ $^{[M+Na]^+}$: 269.1512; Found: 269.1484.

(5d) ethyl (Z)-4-ethyl-2-phenyloct-2-enoate

The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (2a) with 2-ethylhexanal (1d) and benzene (3a), and purified by flash column chromatography as colorless oil (41.6 mg, 76%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34 – 7.28 (m, 5H), 5.85 (dd, $J = 10.4$, 0.8 Hz, 1H), 4.31 – 4.26 (m, 2H), 2.62 – 2.55 (m, 1H), 1.55 – 1.48 (m, 2H), 1.29 (dd, $J = 7.2$, 6 Hz, 9H), 0.92 – 0.89 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.80, 143.39, 138.02, 134.98, 128.44, 127.60, 127.05, 60.78, 41.68, 35.12, 29.75, 28.50, 23.02, 14.42, 14.21, 11.98. IR (cm$^{-1}$): 3085, 3029, 2928, 2873, 1722, 1643, 748. HRMS: calcd. for C$_{17}$H$_{23}$NaO$_2$ $^{[M+Na]^+}$: 297.1825; Found: 297.1803.

(5e) ethyl (Z)-2,4-diphenylpent-2-enoate

The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (2a) with 2-ethylhexanal (1d) and benzene (3a), and purified by flash column chromatography as colorless oil (41.6 mg, 76%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34 – 7.28 (m, 5H), 5.85 (dd, $J = 10.4$, 0.8 Hz, 1H), 4.31 – 4.26 (m, 2H), 2.62 – 2.55 (m, 1H), 1.55 – 1.48 (m, 2H), 1.29 (dd, $J = 7.2$, 6 Hz, 9H), 0.92 – 0.89 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.80, 143.39, 138.02, 134.98, 128.44, 127.60, 127.05, 60.78, 41.68, 35.12, 29.75, 28.50, 23.02, 14.42, 14.21, 11.98. IR (cm$^{-1}$): 3085, 3029, 2928, 2873, 1722, 1634, 748. HRMS: calcd. for C$_{17}$H$_{23}$NaO$_2$ $^{[M+Na]^+}$: 297.1825; Found: 297.1803.
The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (2a) with 2-phenylpropanal (1e) and benzene (3a), and purified by flash column chromatography as yellow oil (41.4 mg, 74%).

\[ \text{1H NMR (400 MHz, CDCl}_3\text{)} \delta 7.34 – 7.28 (m, 10H), 6.19 (d, J = 10.4 Hz, 1H), 4.32 (q, J = 7.2 Hz, 2H), 4.21 – 4.14 (m, 1H), 1.48 (d, J = 6.8 Hz, 3H), 1.32 (t, J = 7.2 Hz, 3H). \]

\[ \text{13C NMR (100 MHz, CDCl}_3\text{)} \delta 168.39, 144.74, 142.73, 137.64, 133.27, 128.72, 128.42, 127.80, 127.19, 126.55, 61.04, 39.66, 21.33, 14.41. \]

IR (cm\(^{-1}\)): 3244, 3085, 3029, 2928, 2873, 1722, 748.

(5f) ethyl (Z)-2,4-diphenylbut-2-enoate

The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (2a) with 2-phenylpropanal (1e) and benzene (3a), and purified by flash column chromatography as colorless oil (28.7 mg, 54%).

\[ \text{1H NMR (400 MHz, CDCl}_3\text{)} \delta 7.35 – 7.27 (m, 10H), 6.29 (t, J = 7.6 Hz, 1H), 4.34 (q, J = 7.2 Hz, 2H), 3.76 (t, J = 8.6 Hz, 2H), 1.34 (t, J = 7.2 Hz, 3H). \]

\[ \text{13C NMR (100 MHz, CDCl}_3\text{)} \delta 168.32, 147.42, 137.18, 129.15, 128.93, 128.80, 128.75, 128.43, 127.84, 127.27, 126.52, 61.09, 36.41, 14.42. \]

IR (cm\(^{-1}\)): 3125, 3112, 2948, 2893, 1732, 1635, 755.

(5g) ethyl (Z)-5-methyl-2-phenylhex-2-enoate

The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (2a) with 3-methylbutanal (1g) and benzene (3a), and purified by flash column chromatography as colorless oil (29.2 mg, 63%).

\[ \text{1H NMR (400 MHz, CDCl}_3\text{)} \delta 7.34 – 7.28 (m, 5H), 6.19 (t, J = 7.6 Hz, 1H), 4.30 (q, J = 7.2 Hz, 2H), 4.30 (t, J = 7.2 Hz, 2H), 1.85 – 1.75 (m, 1H), 1.32 (t, J = 7.0 Hz, 3H), 0.97 (d, J = 6.4 Hz, 6H). \]

\[ \text{13C NMR (100 MHz, CDCl}_3\text{)} \delta 168.55, 138.44, 138.09, 135.45, 128.42, 127.62, 127.18, 60.84, 39.07, 28.93, 22.61, 14.43. \]

IR (cm\(^{-1}\)): 3085, 3062, 2957, 2869, 1721, 1636, 754. HRMS: calcd. for C\(_{15}\)H\(_{20}\)NaO\(_2\)^+ [M+Na]^+: 255.1356; Found: 255.1368.

(5h) ethyl (E)-2-phenylpent-2-enoate

The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (2a) with propionaldehyde (1h) and benzene (3a), and purified by flash column chromatography as colorless oil (22.9 mg, 56% (Z:E = 1:9)).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38 – 7.30 (m, 5H), 7.04 (t, $J = 7.6$ Hz, 1H), 4.20 (q, $J = 7.2$ Hz, 2H), 2.13 – 2.04 (m, 2H), 1.26 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.44, 146.37, 139.76, 129.90, 129.79, 128.00, 127.40, 60.87, 23.01, 14.34, 13.46. IR (cm$^{-1}$): 3083, 3072, 2950, 2871, 1732, 1633, 755.

(5i) (E)-4-ethoxy-4-oxo-3-phenylbut-2-en-1-yl benzoate

\[ \text{Ph} \quad \text{O} \quad \text{CO}_2\text{Et} \]

The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (2a) with 2-oxoethyl benzoate (1i) and benzene (3a), and purified by flash column chromatography as colorless oil (42.1 mg, 68%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.07 (t, $J = 4.2$ Hz, 2H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.45 (dd, $J = 6.4$ Hz, 4H), 7.42 – 7.41 (m, 2H), 7.39 – 7.35 (m, 2H), 5.37 (s, 2H), 4.31 (dq, $J = 53.6$, 7.2 Hz, 2H), 1.28 (dd, $J = 14.0$, 7.2 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 178.94, 166.59, 136.19, 133.18, 130.26, 129.85, 129.51, 128.95, 128.74, 128.52, 128.31, 128.22, 66.84, 61.90, 14.30. IR (cm$^{-1}$): 3065, 3033, 2926, 2956, 2853, 1720, 1654, 735. HRMS: calcd. for C$_{18}$H$_{16}$NaO$_4^+$ [M+Na]$^+$: 333.1097; Found: 333.1090.

(5j) ethyl (E)-2-phenylhex-2-enoate

\[ \text{CO}_2\text{Et} \quad \text{Ph} \quad \text{O} \]

The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (2a) with cyclopropanecarbaldehyde (1j) and benzene (3a), and purified by flash column chromatography as colorless oil (18.7 mg, 43%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38 – 7.29 (m, 3H), 7.18 – 7.16 (m, 2H), 7.06 (t, $J = 7.6$ Hz, 1H), 4.20 (q, $J = 7.2$ Hz, 2H), 2.06 (dd, $J = 14.8$, 7.6 Hz, 2H), 1.45 (dd, $J = 14.8$, 7.2 Hz, 2H), 1.26 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.49, 145.06, 135.69, 134.20, 129.89, 128.03, 127.40, 60.92, 31.63, 22.28, 14.40, 14.00. IR (cm$^{-1}$): 3012, 3001, 2958, 2837, 1736, 1073, 749. HRMS: calcd. for C$_{14}$H$_{18}$NaO$_2^+$ [M+Na]$^+$: 225.1244; Found: 225.1253.

(5k) ethyl (Z)-4-methyl-2-phenylpent-2-enoate

\[ \text{CO}_2\text{Et} \quad \text{Ph} \]

The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (2a) with isobutyraldehyde (1k) and benzene (3a), and purified by flash column chromatography as colorless oil (34.9 mg, 80%).
\[\text{H NMR (400 MHz, CDCl}_3\] \(\delta\) 7.38 – 7.29 (m, 4H), 7.17 (d, \(J = 7.2\) Hz, 1H), 6.84 (d, \(J = 10.8\) Hz, 0.7×1H), 5.95 (d, \(J = 10.0\) Hz, 0.3×1H), 4.32 – 4.27 (m, 0.65×1H), 4.22 – 4.17 (m, 1.35×1H), 2.97 – 2.88 (m, 1H), 2.45 – 2.36 (m, 2H), 1.32 (t, \(J = 7.0\) Hz, 1H), 1.26 (t, \(J = 6.6\) Hz, 2H), 1.10 (d, \(J = 6.4\) Hz, 2H), 0.99 (d, \(J = 6.4\) Hz, 4H). \[\text{13C NMR (100 MHz, CDCl}_3\] \(\delta\) 168.62, 167.62, 151.32, 145.47, 137.74, 135.80, 132.68, 131.84, 129.91, 129.66, 128.39, 128.03, 127.59, 127.37, 127.07, 60.92, 60.86, 29.56, 28.64, 22.83, 22.33, 14.35. IR (cm\(^{-1}\)): 3012, 3001, 2958, 2837, 1736, 1073, 749.

(5l) ethyl (Z)-3-(2,2-dimethyl-1,3-dioxolan-4-yl)-2-phenylacrylate

![Image of ethyl (Z)-3-(2,2-dimethyl-1,3-dioxolan-4-yl)-2-phenylacrylate]

The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (2a) with 2,2-dimethyl-1,3-dioxolane-4-carbaldehyde (II) and benzene (3a), and purified by flash column chromatography as colorless oil (39.7 mg, 72%).

\[\text{H NMR (400 MHz, CDCl}_3\] \(\delta\) 7.35 – 7.30 (m, 5H), 6.27 (d, \(J = 7.2\) Hz, 1H), 5.14 (q, \(J = 7.2\) Hz, 1H), 4.35 (dd, \(J = 8.4, 6.8\) Hz, 1H), 4.32 – 4.26 (m, 2H), 3.74 (dd, \(J = 8.4, 7.2\) Hz, 1H), 1.44 (d, \(J = 19.6\) Hz, 6H), 1.31 (t, \(J = 7.2\) Hz, 3H). \[\text{13C NMR (100 MHz, CDCl}_3\] \(\delta\) 167.19, 139.88, 136.96, 136.38, 128.44, 128.30, 127.83, 109.96, 74.32, 69.83, 61.39, 26.75, 25.77, 14.36. IR (cm\(^{-1}\)): 3433, 3031, 2985, 2935, 2874, 1716, 1637, 761. HRMS: calcd. for C\(_{15}\)H\(_{17}\)NaO\(_4\): [M+Na]\(^{+}\): 299.1254; Found: 299.1267.

(5m) Ethyl(Z)-2-phenyl-3-(2,2,7,7-tetramethyltetrahydro-5H-bis[1,3]dioxolo)[4,5-b:4’,5’-d]pyran-5-yl)acrylate\(^6\)

![Image of Ethyl(Z)-2-phenyl-3-(2,2,7,7-tetramethyltetrahydro-5H-bis[1,3]dioxolo)[4,5-b:4’,5’-d]pyran-5-yl)acrylate]

The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (2a) with D-galactopyranose (1m) and benzene (3a), and purified by flash column chromatography as colorless oil (48.5 mg, 72%, d.r. = 1:1).

\[\text{H NMR (400 MHz, CDCl}_3\] \(\delta\) 7.43 – 7.29 (m, 5H), 6.28 (d, \(J = 8.0\) Hz, 0.5×1H), 6.08 (d, \(J = 7.2\) Hz, 0.5×1H), 5.59 (d, \(J = 5.2\) Hz, 0.5×1H), 5.33 (d, \(J = 2.4\) Hz, 0.5×1H), 5.05 (dd, \(J = 8.0, 2.0\) Hz, 0.5×1H), 4.71 – 4.66 (m, 0.5×1H), 4.59 (dd, \(J = 5.2, 3.6\) Hz, 0.5×1H), 4.50 (dd, \(J = 7.6, 2.0\) Hz, 0.5×1H), 4.40 – 4.35 (m, 1H), 4.33 – 4.27 (m, 2H), 4.24 (dd, \(J = 8.8, 5.2\) Hz, 0.5×1H), 4.09 (dd, \(J = 9.6, 5.2\) Hz, 0.5×1H), 1.58 – 1.48 (m, 6H), 1.44 – 1.36 (m, 6H), 1.34 – 1.26 (m, 3H). \[\text{13C NMR (100 MHz, CDCl}_3\] \(\delta\) 166.40, 138.87, 137.73, 134.54, 129.77, 127.98, 111.01, 109.10, 100.01, 96.25, 75.53, 74.18, 72.96, 70.30, 61.26, 27.97, 27.11, 25.84, 25.60, 14.20. HRMS: calcd. for C\(_{21}\)H\(_{22}\)NaO\(_7\): [M+Na]\(^{+}\): 427.1727; Found: 427.1775.
(6b) ethyl (Z)-2-(2,5-dimethylphenyl)-4,4-dimethylpent-2-enoate

The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (2a) with pivalaldehyde (1a) and p-xylene (3b), and purified by flash column chromatography as colorless oil (38.5 mg, 74%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.12 (s, 1H), 7.06 – 6.98 (m, 2H), 5.59 (s, 1H), 4.17 (d, $J = 7.2$ Hz, 2H), 2.30 (t, $J = 9.4$ Hz, 6H), 1.27 (t, $J = 7.0$ Hz, 3H), 1.19 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.64, 146.64, 139.06, 135.19, 130.24, 130.13, 129.43, 128.63, 128.45, 60.85, 33.97, 29.92, 20.98, 19.56, 14.18. IR (cm$^{-1}$): 3098, 3017, 2957, 2868, 1721, 1683, 1646, 747.

HRMS: calcd. for C$_{16}$H$_{22}$O$_2^{+}$ [M+H]$^+$: 247.1693; Found: 247.1689.

(6c) ethyl (Z)-2-(2,5-bis(trifluoromethyl)phenyl)-4,4-dimethylpent-2-enoate

The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (2a) with pivalaldehyde (1a) and 1,4-bis(trifluoromethyl)benzene (3c), and purified by flash column chromatography as colorless oil (53.7 mg, 73%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.80 – 7.65 (m, 3H), 5.84 (s, 1H), 4.18 (q, $J = 7.2$ Hz, 2H), 1.25 (s, 3H), 1.24 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.23, 156.95, 147.20, 144.73, 142.94, 120.42, 119.01 (t, $J = 9.2$ Hz), 105.10 (t, $J = 89.6$ Hz), 61.41, 34.75, 29.75, 14.02. IR (cm$^{-1}$): 2961, 2929, 2872, 2856, 1731, 1647, 753. HRMS: calcd. for C$_{16}$H$_{15}$F$_6$NaO$_2^{+}$ [M+Na]$^+$: 391.1103; Found: 391.1120.

(6d) ethyl (Z)-2-(2,5-dichlorophenyl)-4,4-dimethylpent-2-enoate

The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (2a) with pivalaldehyde (1a) and 1,4-dichlorobenzene (3d), and purified by flash column chromatography as colorless oil (55.8 mg, 93%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.27 (dd, $J = 8.8$, 2.8 Hz, 2H), 7.19 (dd, $J = 8.4$, 2.4 Hz, 1H), 5.94 (s, 1H), 4.21 (q, $J = 7.2$ Hz, 2H), 1.28 (d, $J = 7.2$ Hz, 3H), 1.25 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.26, 152.51, 140.46, 132.51, 131.75, 131.22, 130.66, 129.99, 128.88, 61.17, 34.22, 29.88, 14.10. IR (cm$^{-1}$): 3018, 2989, 2876, 2813, 1712, 1688, 748. HRMS: calcd. for C$_{16}$H$_{15}$Cl$_2$NaO$_2^{+}$ [M+Na]$^+$: 323.0576; Found: 323.0570.
(6e) ethyl (Z)-2-(2,5-dibromophenyl)-4,4-dimethylpent-2-enoate

The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (2a) with pivalaldehyde (1a) and 1,4-dibromobenzene (3e), and purified by flash column chromatography as colorless oil (65.0 mg, 84%).

1H NMR (400 MHz, CDCl₃) δ 7.42 (dd, J = 10.0, 2.4 Hz, 2H), 7.26 (dd, J = 8.4, 2.0 Hz, 1H), 5.89 (s, 1H), 4.20 (q, J = 7.2 Hz, 2H), 1.27 (d, J = 7.2 Hz, 3H), 1.25 (s, 9H). 13C NMR (100 MHz, CDCl₃) δ 166.94, 152.72, 142.73, 134.14, 134.03, 131.99, 131.31, 122.34, 121.07, 61.17, 34.17, 29.81, 14.11. IR (cm⁻¹): 3016, 2957, 2870, 2844, 1719, 1648, 754.


(6f) ethyl (Z)-2-(2,3-dichlorophenyl)-4,4-dimethylpent-2-enoate

The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (2a) with pivalaldehyde (1a) and 1,2-dichlorobenzene (3f), and purified by flash column chromatography as colorless oil (47.4 mg, 79% (α:β = 1:1)).

1H NMR (400 MHz, CDCl₃) δ 7.42 – 7.36 (m, 1.5×1H), 7.21 – 7.14 (m, 4.0 Hz, 1.5×1H), 5.93 (s, 0.5×1H), 5.90 (s, 0.5×1H), 4.31 – 4.18 (m, 2H), 1.35 – 1.26 (m, 3H), 1.21 (d, J = 26.8 Hz, 9H). 13C NMR (100 MHz, CDCl₃) δ 169.17, 167.40, 152.17, 144.31, 141.32, 138.20, 133.17, 132.70, 131.90, 131.73, 130.81, 130.45, 129.73, 129.67, 128.17, 127.24, 125.57, 121.70, 121.07, 61.44, 61.13, 34.20, 34.15, 29.88, 29.73, 14.14, 14.10. IR (cm⁻¹): 3019, 2961, 2906, 2870, 1720, 1635, 743. HRMS: calcd. for C₁₄H₁₅Cl₂NaO₂⁺ [M+Na]⁺: 323.0576; Found: 323.0557.

(6g) ethyl (Z)-2-mesityl-4,4-dimethylpent-2-enoate

The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (2a) with pivalaldehyde (1a) and mesitylene (3g), and purified by flash column chromatography as colorless oil (35.1 mg, 64%).

1H NMR (400 MHz, CDCl₃) δ 6.85 (s, 2H), 5.49 (s, 1H), 4.13 (q, J = 6.8 Hz, 2H), 2.27 (d, J = 7.2 Hz, 9H), 1.24 (t, J = 7.2 Hz, 3H), 1.20 (s, 9H). 13C NMR (100 MHz, CDCl₃) δ 169.24, 147.33, 137.14, 136.93, 136.16, 130.14, 128.28, 60.64, 33.91, 29.83, 21.13, 20.30, 14.18. IR (cm⁻¹): 3098,

(6h) ethyl (Z)-4,4-dimethyl-2-(2,4,6-tribromophenyl)pent-2-enoate

The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (2a) with pivalaldehyde (1a) and 1,3,5-tribromobenzene (3h), and purified by flash column chromatography as yellow oil (53.0 mg, 57%).

1H NMR (400 MHz, CDCl₃) δ 7.66 (d, J = 36.4 Hz, 2H), 5.94 (s, 1H), 4.17 (q, J = 7.2 Hz, 2H), 1.31 (s, 9H), 1.22 (t, J = 7.2 Hz, 3H). 13C NMR (100 MHz, CDCl₃) δ 164.65, 158.11, 140.94, 134.22, 133.15, 130.96, 125.70, 121.72, 60.93, 34.16, 29.66, 14.15. IR (cm⁻¹): 3105, 3056, 2976, 2870, 1698, 1639, 748. HRMS: calcd. for C₁₄H₁₅Br₃O₂⁺ [M+H]⁺: 466.8851; Found: 466.8851.

(6i) ethyl (Z)-4,4-dimethyl-2-(2,3,5,6-tetrafluorophenyl)pent-2-enoate

The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (2a) with pivalaldehyde (1a) and 1,2,4,5-tetrafluorobenzene (3i), and purified by flash column chromatography as yellow oil (40.1 mg, 66%).

1H NMR (400 MHz, CDCl₃) δ 7.03 – 6.98 (m, 1H), 6.17 (s, 1H), 4.23 (d, J = 7.2 Hz, 2H), 1.29 (d, J = 7.2 Hz, 3H), 1.27 (s, 9H). 13C NMR (100 MHz, CDCl₃) δ 166.78, 152.52, 139.86, 128.95, 128.38, 127.04, 124.60, 121.72, 60.93, 34.16, 29.66, 14.15. IR (cm⁻¹): 3108, 3093, 2976, 2870, 1698, 1639, 748. HRMS: calcd. for C₁₄H₁₃Br₃O₂⁺ [M+Na]⁺: 327.0979; Found: 327.0970.

(6j) ethyl (Z)-4,4-dimethyl-2-(phenyl-d₅)pent-2-enoate

The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (2a) with pivalaldehyde (1a) and benzene-d₅ (3j), and purified by flash column chromatography as yellow oil (18.8 mg, 79%).
\[^{1}\text{H} \text{NMR (400 MHz, CDCl}_3\] \(\delta\) 5.90 (s, 1H), 4.28 (q, \(J = 7.2\) Hz, 2H), 1.33 (t, \(J = 7.2\) Hz, 3H), 1.19 (s, 9H). \[^{13}\text{C} \text{NMR (100 MHz, CDCl}_3\] \(\delta\) 170.11, 142.49, 137.94, 132.24, 128.11, 127.87 (t, \(J = 48.4\) Hz), 125.71 (t, \(J = 48.2\) Hz), 61.12, 34.04, 29.90, 14.20. IR (cm\(^{-1}\))): 3093, 3039, 2915, 2820, 1727, 1540, 755. HRMS: calcd. for C\(_{14}\)H\(_{12}\)D\(_5\)NaO\(_2\)\([\text{M+Na}]^+\): 260.1669; Found: 260.1670.

\((6k)\) ethyl (Z)-4,4-dimethyl-2-(p-tolyl)pent-2-enoate\(^7,8\)

\[\text{CO}_2\text{Et}\]
\[\text{o}\]
\[\text{m}\]
\[\text{p}\]

The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (2a) with pivaldehyde (1a) and toluene (3k), and purified by flash column chromatography as colorless oil (34.4 mg, 70%, \(\alpha:m:p = 6:2:1\)).

\[^{1}\text{H} \text{NMR (400 MHz, CDCl}_3\] \(\delta\) 7.22 – 7.11 (m, 4H), 5.88 (s, 0.2× 1H), 5.86 (s, 0.1× 1H), 5.60 (s, 0.6× 1H), 4.29 – 4.14 (m, 2H), 2.33 (d, \(J = 6.8\) Hz, 3H), 1.33 – 1.24 (m, 3H), 1.20 – 1.18 (m, 9H). \[^{13}\text{C} \text{NMR (100 MHz, CDCl}_3\] \(\delta\) 169.52, 146.89, 146.73, 142.36, 141.73, 139.33, 136.42, 131.75, 130.33, 129.57, 129.33, 128.53, 127.71, 126.86, 126.02, 125.75, 123.28, 60.86, 34.00, 29.91, 20.06, 14.18. IR (cm\(^{-1}\))): 3053, 3019, 2910, 2872, 1717, 1640, 754. HRMS: calcd. for C\(_{14}\)H\(_{18}\)O\(_2\)\([\text{M+H}]^+\): 247.1693; Found: 247.1689.

\((6l)\) ethyl (Z)-2-((1,1'-biphenyl)-4-yl)-4,4-dimethylpent-2-enoate\(^8\)

\[\text{CO}_2\text{Et}\]
\[\text{o}\]
\[\text{m}\]
\[\text{Ph}\]
\[\text{p}\]

The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (2a) with pivaldehyde (1a) and 1,1'-biphenyl (3m), and purified by flash column chromatography as colorless oil (50.5 mg, 82%, \(\alpha:p = 5:3\)).

\[^{1}\text{H} \text{NMR (400 MHz, CDCl}_3\] \(\delta\) 7.56 (dd, \(J = 12.0, 7.6\) Hz, 3H), 7.45 – 7.33 (m, 6H), 5.69 (d, \(J = 225.2\) Hz, 1H), 4.34 – 4.00 (m, 2H), 1.37 – 1.32 (m, 2.5× 1H), 1.20 (s, 6H), 1.18 (s, 0.5× 1H), 0.94 (s, 3H). \[^{13}\text{C} \text{NMR (100 MHz, CDCl}_3\] \(\delta\) 169.52, 146.89, 146.73, 142.36, 141.73, 139.33, 136.42, 131.75, 130.33, 129.57, 129.33, 128.53, 127.71, 126.86, 126.02, 125.75, 123.28, 60.86, 34.00, 29.91, 20.06, 14.18. IR (cm\(^{-1}\))): 3053, 3019, 2910, 2872, 1717, 1640, 754. HRMS: calcd. for C\(_{21}\)H\(_{25}\)O\(_2\)\([\text{M+H}]^+\): 309.1849; Found: 309.1850.

\((6m)\) ethyl (Z)-4,4-dimethyl-2-(naphthalen-1-yl)pent-2-enoate\(^8,9\)

\[\text{CO}_2\text{Et}\]
\[\text{p}\]
\[\text{a}\]


The title compound was prepared according to the general procedure described above by the reaction between ethyl propiolate (2a) with pivalaldehyde (1a) and naphthalene (3n), and purified by flash column chromatography as colorless oil (34.4 mg, 61%, α:β= 1:5)

1H NMR (400 MHz, CDCl₃) δ 8.18 – 7.78 (m, 3H), 7.52 – 7.42 (m, 4H), 5.92 (d, J = 101.6 Hz, 1H), 4.24 (dq, J = 70.4, 7.2 Hz, 2H), 1.22 (q, J = 7.2 Hz, 12H). 13C NMR (100 MHz, CDCl₃) δ 169.66, 147.83, 137.25, 133.81, 132.10, 130.76, 128.29, 128.16, 126.88, 126.26, 125.89, 125.82, 125.39, 61.04, 34.24, 29.96, 14.13. IR (cm⁻¹): 3132, 3059, 2917, 2826, 1712, 1620, 755. HRMS: calcd. for C₁₉H₂₃O₂⁺ [M+H]⁺: 283.1693; Found: 283.1692.

VIII. References


IX. Copies of ¹H and ¹³C NMR spectra of products 4a-4i, 5b-5m, 6b-6m
5m (Z, d.r. = 1:1)
$5m$ (Z, d.r. = 1:1)