Support Information

Reaction of Trisubstituted Alkenes with Iron Porphyrin Carbenes: Facile Synthesis of Tetrasubstituted Dienes and Cyclopentadienes

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**General Information** All reactions were carried out under N\textsubscript{2} unless otherwise noted. All carbonyl compounds and solvents were purified according to standard methods unless otherwise noted.

\textsuperscript{1}H NMR spectra were recorded on a VARIAN Mercury 300 MHz or VARIAN Mercury 400 MHz spectrometer in chloroform-d. All signals are reported in ppm with the internal TMS signal at 0.0 ppm or chloroform signal at 7.26 ppm as a standard. The data are reported as (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet or unresolved, coupling constant(s) in Hz, integration). \textsuperscript{13}C NMR spectra were recorded on a VARIAN Mercury 75.5 MHz spectrometer in chloroform-d. All signals are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard. IR spectra were recorded on a Perkin–Elmer 983, Digital FT–IR spectrometer or Bruker–Tensor 27; frequencies are given in reciprocal centimeters (cm\textsuperscript{-1}) and only selected absorbance is reported; Mass spectra were determined on an Agilent 5973N MSD (EI) and Shimadzu LCMS-2010EV (ESI) mass spectrometer or Agilent G6100 LC/MSD (ESI) single Quand mass spectrometer. High resolution mass spectra were recorded on Waters Micromass GCT Premier (EI) and Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS (ESI) mass spectrometers.

Fe(TCP)Cl\textsubscript{2} was synthesized according to literature procedure.\textsuperscript{1}
2. General Procedures for the Substituent Effect

To a stirred suspension of phosphonium salt 1 (0.5 mmol) in dry PhCH₃ (2.0 mL) under N₂ at room temperature was added LiHMDS (0.6 mL, 1.0 M in THF, 0.6 mmol) in one portion. 10 minutes later, Fe(TCP)Cl (1.7 mg, 0.002 mmol) and MDA (50 µL, 0.6 mmol) were added to the system respectively (Caution! N₂ Release!), then washed the Schlenk tube with dry PhCH₃ (1.0 mL), and the mixture stirred at room temperature for another 10 minutes. PCBA (56.0 mg, 0.4 mmol) and PhCH₃ (1.0 mL) were added and the resulting mixture was stirred at room temperature. After the reaction was complete, the resulting mixture was filtered rapidly through a funnel with a thin layer of silica gel and eluted with DCM. The filtrate was concentrated and analyzed by ¹H NMR, and then the residue was purified by chromatography on silica gel to afford the desired products.

For 1a and 1b, No desired products were formed.

For 1c, desired product 3a was isolated in 13% yield, 3E,5E/3E,5Z = 69/31.

(3E, 5E)-3a, white solid, ¹H NMR (CDCl₃, 400 MHz) δ 8.03 (d, J = 16.0 Hz, 1H), 7.41 (d, J = 8.8 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 16.0 Hz, 1H), 3.80 (s, 3H), 3.70 (s, 3H), 3.55 (s, 2H), 2.09 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 171.2, 167.9, 145.5, 135.6, 133.9, 132.3, 128.8, 128.6, 128.3, 123.1, 52.1, 51.9, 36.1, 16.2; IR (neat) ν 2951 (m), 2847 (m), 1736 (s), 1706 (s), 1191 (s), 1166 (m), 965 (m), 812 (s); MS (EI, m/z, rel. intensity) 308 (52, M⁺), 293 (2.5), 277 (12), 248 (13), 235 (15), 217 (24), 203 (57), 189 (60), 171 (9.7), 153 (31), 127 (32), 113 (33), 99 (31), 84 (57), 71 (68), 57 (100), 43 (60), 41 (24); HRMS (EI) calcd for C₁₆H₁₇ClO₄(M⁺): 308.0815; Found: 308.0811.
For 1d, desired product 4a was isolated in 49% yield, 3E,5E/3E,5Z = 83/17, the direct Wittig reaction of phosphonium salt 1d was also observed.

\[
\begin{align*}
\text{For } 1d, \text{ desired product } 4a \text{ was isolated in } 49\% \text{ yield, } 3E,5E/3E,5Z &= 83/17, \text{ the direct Wittig reaction of phosphonium salt } 1d \text{ was also observed.}
\end{align*}
\]

19% yield, white solid, \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.07 (d, \(J = 16.0 \text{ Hz}, 1\text{H}), 7.46 (dt, \(J = 2.2, 8.8 \text{ Hz}, 2\text{H}), 7.30 (dt, \(J = 2.2, 8.4 \text{ Hz}, 2\text{H}), 7.22 (d, \(J = 16.0 \text{ Hz}, 1\text{H}), 5.16 (s, 1\text{H}), 3.74 (s, 3\text{H}), 3.72 (s, 3\text{H}); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 167.7, 166.5, 134.6, 134.5, 133.8, 128.8, 128.7, 120.6, 92.1, 55.4, 50.9; IR (neat) \(\nu\) 2951 (m), 2847 (m), 1703 (m), 1583 (s), 1566 (m), 1490 (m), 1433 (m), 1145 (s), 970 (s); MS (EI, m/z, rel. intensity) 252 (28, M\(^+\)), 221 (17), 192 (100), 178 (20), 158 (61), 149 (14), 127 (22), 115 (36), 101 (17), 89 (5.5), 75 (12), 59 (13); HRMS (EI) calcd for C\(_{13}\)H\(_{13}\)ClO\(_3\) (M\(^+\)): 252.0553; Found: 252.0556.

4% yield, White solid, \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.25 (d, \(J = 8.8 \text{ Hz}, 2\text{H}), 7.18 (d, \(J = 8.8 \text{ Hz}, 2\text{H}), 6.95 (d, \(J = 12.8 \text{ Hz}, 1\text{H}), 6.68 (d, \(J = 12.8 \text{ Hz}, 1\text{H}, 5.19 (s, 1\text{H}), 3.71 (s, 3\text{H}), 3.54 (s, 3\text{H}).
40% yield, colorless liquid, $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.78 (d, $J = 16.0$ Hz, 1H), 7.45 (d, $J = 8.0$ Hz, 2H), 7.32 (d, $J = 7.2$ Hz, 2H), 6.98 (d, $J = 16.4$ Hz, 1H), 3.76 (s, 3H), 3.73 (s, 3H), 3.70 (s, 3H), 3.54 (s, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 171.8, 167.5, 164.9, 134.5, 134.4, 128.8, 128.5, 121.1, 113.4, 60.5, 51.9, 51.7, 32.6; IR (neat) $\nu$ 2954 (m), 1735 (s), 1610 (m), 1589 (m), 1565 (m), 1491 (m), 1436 (m); MS (EI, m/z, rel. intensity) 324 (1.2, M$^+$), 310 (2.3), 293 (1.8), 279 (2.7), 265 (4.1), 251 (12), 233 (9.6), 219 (36), 205 (14), 165 (100), 137 (20), 102 (24), 75 (8.7), 59 (11); HRMS (EI) calcd for C$_{16}$H$_{17}$ClO$_5$ (M$^+$): 324.0765; Found: 324.0763.

9% yield, colorless liquid, $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.40-7.38 (m, 2H), 7.29-7.27 (m, 2H), 6.68 (d, $J = 12.4$ Hz, 1H), 6.45 (d, $J = 12.8$ Hz, 1H), 3.72 (s, 3H), 3.68 (s, 3H), 3.48 (s, 2H), 3.46 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 172.1, 167.5, 164.1, 134.2, 133.0, 130.1, 128.6, 121.7, 106.2, 56.5, 51.8, 51.4, 31.5; IR (neat) $\nu$ 2953 (m), 1738 (s), 1587 (m), 1491 (m), 1437 (m); MS (EI, m/z, rel. intensity) 324 (0.7, M$^+$), 293 (5.1), 265 (10), 251 (31), 233 (26), 219 (100), 205 (38), 165 (9.8), 139 (12), 102 (10), 75 (8.1), 59 (17); HRMS (EI) calcd for C$_{16}$H$_{17}$ClO$_5$ (M$^+$): 324.0765; Found: 324.0773.
3. Reaction Conditions for Synthesis of Tetrasubstituted Dienes

**Table S1.** Base and solvent effect on the reaction.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>Solvent</th>
<th>(3E, 5E)-4a (%)</th>
<th>3E, 5E/3E, 5Z</th>
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<tr>
<td>1</td>
<td>LiHMDS</td>
<td>THF</td>
<td>13</td>
<td>83/17</td>
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<tr>
<td>2</td>
<td>NaHMDS</td>
<td>THF</td>
<td>39</td>
<td>97/3</td>
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<tr>
<td>3</td>
<td>CH(_3)ONa</td>
<td>THF</td>
<td>48</td>
<td>98/2</td>
</tr>
<tr>
<td>4</td>
<td>K(_2)CO(_3)</td>
<td>THF</td>
<td>30</td>
<td>84/16</td>
</tr>
<tr>
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<td>(t)-BuOK</td>
<td>THF</td>
<td>78</td>
<td>97/3</td>
</tr>
<tr>
<td>6</td>
<td>(t)-BuOK</td>
<td>DME</td>
<td>85</td>
<td>98/2</td>
</tr>
<tr>
<td>7</td>
<td>(t)-BuOK</td>
<td>CH(_2)Cl(_2)</td>
<td>84</td>
<td>99/1</td>
</tr>
<tr>
<td>8</td>
<td>(t)-BuOK</td>
<td>PhCH(_3)</td>
<td>81</td>
<td>95/5</td>
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</tr>
<tr>
<td>10</td>
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<td>CH(_3)CN</td>
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<td>99/1</td>
</tr>
<tr>
<td>11</td>
<td>(t)-BuOK</td>
<td>CH(_3)CN</td>
<td>85</td>
<td>98/2</td>
</tr>
</tbody>
</table>

\(^a\) Phosphonium salt 1d (235.5 mg, 0.5 mmol), base (0.6 mmol), MDA (50 \(\mu\)L, 0.6 mmol), PCBA (56 mg, 0.4 mmol), Fe(TCP)Cl (1.7 mg, 0.002 mmol), solvent (4.0 mL).

\(^b\) Isolated yield of single isomer. 

\(^c\) Determined by \(^1\)H NMR. 

\(^d\) Using 0.1 mol\% [Fe(TCP)Cl] as catalyst.
4. General Procedure for Synthesis of Tetrasubstituted Dienes

To a stirred suspension of phosphonium salt 1d (236 mg, 0.5 mmol) in 2.0 mL dry CH₃CN under N₂ at room temperature was added t-BuOK (67.2 mg, 0.60 mmol) in one portion. After 10 min, Fe(TCP)Cl (1.7 mg, 0.002 mmol) and MDA (50 µL, 0.6 mmol) were added to the system respectively (Caution! N₂ Release!), washed the Schlenk tube with 1.0 mL dry CH₃CN, and the mixture stirred for another 10 min. Aldehyde (0.4 mmol) and CH₃CN (1.0 mL) were added and the resulting mixture was stirred at room temperature. After the reaction was complete, the resulting mixture was filtered rapidly through a funnel with a thin layer of silica gel and eluted with DCM. The filtrate was concentrated and the residue was purified by chromatography on silica gel to afford the desired products.

86% yield, white solid, ¹H NMR (CDCl₃, 300 MHz) δ 7.79 (d, J = 16.2 Hz, 1H), 7.48 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.7 Hz, 2H), 6.97 (d, J = 15.9 Hz, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 3.71 (s, 3H), 3.53 (s, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 171.8, 167.5, 164.9, 134.9, 134.5, 131.7, 128.8, 122.8, 121.2, 113.4, 60.5, 51.8, 51.7, 32.5; IR (KBr) ν 2954 (m), 1734 (s), 1609 (m), 1584 (m), 1487 (m), 1438 (m), 1256 (m), 1205 (m), 1170 (m); MS (EI, m/z, rel. intensity) 369 (4, M⁺), 337 (12), 309 (13), 295 (45), 279 (23), 265 (100), 249 (30), 235 (4.6), 211 (5.4), 198 (8.4), 183 (8.7), 171 (8.5), 155 (8.2), 141 (10), 128 (18), 115 (10), 102 (19), 75 (7.3), 59 (32), 45 (5.3); HRMS (EI) calcd for C₁₆H₁₇BrO₅ (M⁺): 368.0259; Found: 368.0251.

78% yield, light yellow solid, ¹H NMR (CDCl₃, 400 MHz) δ 8.01-7.99 (m, 1H), 7.80-7.71 (m, 2H), 7.65-7.61 (m, 1H), 7.49-7.43 (m, 2H), 3.83 (s, 3H), 3.77 (s, 3H),
3.72 (s, 3H), 3.56 (s, 2H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 171.7, 167.4, 164.3, 148.0, 133.3, 132.0, 130.9, 128.96, 128.90, 125.2, 124.6, 114.2, 60.4, 51.9, 51.8, 32.4; IR (KBr) v 2952 (m), 1741 (s), 1710 (s), 1586 (m), 1524 (m), 1435 (s), 1346 (m); MS (EI, m/z, rel. intensity) 335 (19, M\(^+\)), 318 (35), 304 (25), 276 (10), 262 (22), 244 (22), 230 (98), 216 (19), 200 (100), 188 (6.0), 170 (8.2), 156 (17), 141 (45), 128 (35), 120 (46), 102 (12), 92 (12), 77 (14), 59 (37), 45 (9.1); HRMS (EI) calcd for C\(_{16}\)H\(_{17}\)NO\(_7\) (M\(^+\)): 335.1005; Found: 335.1004.

83\% yield, light yellow solid, \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.32 (t, \(J = 2.0\) Hz, 1H), 8.15-8.13 (m, 1H), 7.92-7.86 (m, 2H), 7.57-7.53 (m, 1H), 7.08 (d, \(J = 16.8\) Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.72 (s, 3H), 3.56 (s, 2H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 171.5, 167.2, 164.0, 148.5, 137.8, 133.0, 132.5, 129.6, 123.5, 123.0, 122.0, 114.8, 60.5, 51.9, 51.8, 32.6; IR (KBr) v 2953 (m), 1732 (s), 1737 (s), 1705 (s), 1600 (m), 1519 (s), 1435 (m), 1443 (s); MS (EI, m/z, rel. intensity) 335 (6.7, M\(^+\)), 304 (12), 276 (19), 262 (24), 244 (16), 230 (100), 216 (38), 200 (6.2), 184 (3.4), 170 (4.7), 155 (4.3), 141 (5.1), 128 (11), 115 (8.2), 102 (5.9), 89 (1.7), 75 (3.2), 59 (13), 45 (3.2); HRMS (EI) calcd for C\(_{16}\)H\(_{17}\)NO\(_7\) (M\(^+\)): 335.1005; Found: 335.1009.

90\% yield, light yellow solid, \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.20 (d, \(J = 8.4\) Hz, 2H), 7.96 (d, \(J = 16.4\) Hz, 1H), 7.66 (d, \(J = 8.4\) Hz, 2H), 7.08 (d, \(J = 16.0\) Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.72 (s, 3H), 3.57 (s, 2H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 171.5, 167.2, 164.0, 147.3, 142.4, 132.9, 127.8, 124.8, 123.9, 115.4, 60.6, 51.91, 51.87, 32.6; IR (KBr) v 2953 (m), 1732 (s), 1737 (s), 1705 (s), 1600 (m), 1519 (s), 1435 (m), 1443 (s); MS (EI, m/z, rel. intensity) 335 (6.7, M\(^+\)), 304 (12), 276 (19), 262 (24).
(24), 244 (16), 230 (100), 216 (38), 198 (5.9), 186 (3.0), 170 (5.5), 155 (3.3), 141 (3.7), 128 (10), 102 (6.8), 89 (2.0), 75 (2.8), 59 (15), 45 (3.5); HRMS (EI) calcd for C_{16}H_{17}NO_7 (M^+): 335.1005; Found: 335.1009.

\[
\text{(3E, 5E)-4f} 
\]

90% yield, white solid, ^1\text{H} NMR (CDCl_3, 400 MHz) \(\delta 7.78 (d, J = 16.4 \text{ Hz}, 1H), 7.53 (d, J = 7.6 \text{ Hz}, 2H), 7.37-7.27 (m, 3H), 7.04 (d, J = 16.0 \text{ Hz}, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 3.70 (s, 3H), 3.54 (s, 2H); ^13\text{C} \text{NMR (CDCl}_3, 100 MHz) \delta 172.0, 167.6, 165.2, 136.0, 128.8, 128.6, 127.4, 120.4, 112.9, 60.4, 51.8, 51.7, 32.6; IR (KBr) \nu 2955(m), 1732 (s), 1689 (m), 1607 (m), 1575 (m), 1437 (m); MS (EI, m/z, rel. intensity) 290 (3.8, M^+), 259 (9.6), 231 (16), 217 (46), 199 (32), 185 (100), 171 (43), 157 (6.5), 141 (13), 128 (21), 115 (15), 103 (12), 91 (4.0), 77 (9.8), 59 (14), 45 (3.2); HRMS (EI) calcd for C_{16}H_{18}O_5 (M^+): 290.1154; Found: 290.1157.

71% yield, colorless liquid, ^1\text{H} NMR (CDCl_3, 400 MHz) \(\delta 7.67-7.63 (m, 2H), 7.30 (d, J = 16.0 \text{ Hz}, 1H), 7.22-7.17 (m, 3H), 3.76 (m, 6H), 3.71 (s, 3H), 3.54 (s, 2H), 2.40 (s, 3H), ^13\text{C} \text{NMR (CDCl}_3, 100 MHz) \delta 172.0, 167.6, 165.4, 136.4, 134.9, 133.6, 130.4, 128.6, 126.2, 126.0, 121.3, 112.7, 60.4, 51.8, 51.7, 32.6, 19.7; IR (KBr) \nu 2950 (m), 1741(s), 1710 (s), 1619 (m), 1587 (m), 1435 (m); MS (EI, m/z, rel. intensity) 304 (1.2, M^+), 273 (6.7), 245 (12), 231 (47), 213 (19), 199 (100), 185 (32), 153 (26), 128 (12), 115 (24), 105 (4.2), 84 (43), 59 (18), 45 (4.5); HRMS (EI) calcd for C_{17}H_{20}O_5 (M^+): 304.1311; Found: 304.1310.
77% yield, colorless liquid, $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.78 (d, $J$ = 16.0 Hz, 1H), 7.34-7.32 (m, 2H), 7.24 (t, $J$ = 8.0 Hz, 1H), 7.12 (d, $J$ = 7.6 Hz, 1H), 7.02 (d, $J$ = 16.4 Hz, 1H), 3.76 (s, 3H), 3.73 (s, 3H), 3.70 (s, 3H), 3.54 (s, 2H), 2.36 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 172.0, 167.6, 165.4, 138.2, 136.2, 135.8, 129.7, 128.5, 127.9, 124.6, 120.1, 112.6, 60.4, 51.8, 51.6, 32.5, 21.2; IR (KBr) $\nu$ 2950 (s), 2842 (m), 1743 (s), 1712 (s), 1621 (m), 1435 (m); MS (EI, m/z, rel. intensity) 304 (1.9, M$^+$), 273 (4.8), 245 (10), 230 (52), 213 (36), 199 (100), 185 (40), 171 (5.2), 155 (7.9), 141 (10.9), 128 (13), 115 (17), 105 (2.2), 84 (10), 59 (14), 51 (5.3), 45 (2.5); HRMS (EI) calcd for C$_{17}$H$_{20}$O$_5$ (M$^+$): 304.1311; Found: 304.1319.

77% yield, colorless liquid, $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.75 (d, $J$ = 16.0 Hz, 1H), 7.42 (d, $J$ = 8.0 Hz, 2H), 7.16 (d, $J$ = 8.0 Hz, 2H), 7.02 (d, $J$ = 16.0 Hz, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 3.70 (s, 3H), 3.53 (s, 2H), 2.35 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 172.1, 167.7, 165.6, 139.0, 136.0, 133.2, 129.4, 127.4, 119.4, 112.4, 60.5, 51.8, 51.7, 32.6, 21.2; IR (KBr) $\nu$ 2950 (s), 2842 (m), 1741 (s), 1710 (s), 1620 (m), 1585 (m), 1435 (m); MS (EI, m/z, rel. intensity) 304 (2.1, M$^+$), 273 (4.9), 245 (10), 231 (35), 213 (34), 199 (100), 185 (44), 171 (9.2), 155 (14), 128 (16), 115 (24), 105 (4.7), 84 (91), 71 (9.5), 59 (22), 43 (11); HRMS (EI) calcd for C$_{17}$H$_{20}$O$_5$ (M$^+$): 304.1311; Found: 304.1304.

55% yield, colorless liquid, $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.67 (d, $J$ = 16.0 Hz, 1H), 7.48 (d, $J$ = 8.4 Hz, 2H), 7.01 (d, $J$ = 16.4 Hz, 1H), 6.89 (d, $J$ = 9.2 Hz, 2H), 3.83 (s, 3H), 3.76 (s, 3H), 3.74 (s, 3H), 3.70 (s, 3H), 3.53 (s, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 172.2, 167.8, 165.8, 160.3, 135.8, 128.9, 128.8, 118.3, 114.1, 112.0, 60.6,
55.3, 51.9, 51.7, 32.7; IR (KBr) ν 2951 (m), 2840 (m), 1741 (s), 1709 (s), 1602 (m), 1512 (m), 1435 (m); MS (EI, m/z, rel. intensity) 320 (7.2, M⁺), 289 (3.9), 261 (11), 246 (57), 229 (51), 215 (100), 201 (30), 187 (5.6), 171 (6.4), 161 (6.5), 145 (4.9), 128 (9.2), 115 (8.8), 103 (2.2), 89 (3.1), 77 (3.7), 59 (11), 45 (2.9); HRMS (EI) calcd for C₁₇H₂₀O₆ (M⁺): 320.1260; Found: 320.1262.

95% yield, white solid, ¹H NMR (CDCl₃, 300 MHz) δ 7.73 (d, J = 16.8 Hz, 1H), 7.65 (d, J = 8.1 Hz, 1H), 7.41-7.24 (m, 3H), 3.78 (s, 3H), 3.77 (s, 3H), 3.72 (s, 3H), 3.55 (s, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 171.7, 167.4, 164.6, 134.7, 134.5, 132.8, 130.5, 129.4, 127.9, 127.3, 123.2, 114.1, 60.5, 51.9, 51.7, 32.5; IR (KBr) ν 2954 (m), 1734 (s), 1696 (m), 1608 (m), 1581 (m), 1437 (m), 1368 (m); MS (EI, m/z, rel. intensity) 358 (4.3, M⁺), 327 (7.2), 299 (24), 285 (34), 267 (22), 253 (100), 239 (52), 225 (6.4), 211 (4.9), 199 (7.2), 173 (8.8), 162 (11), 139 (11), 113 (7.7), 99 (10), 86 (5.8), 75 (8.8), 59 (44), 49 (10); HRMS (EI) calcd for C₁₆H₁₆Cl₂O₅ (M⁺): 358.0375; Found: 358.0381.

86% yield, colorless liquid, ¹H NMR (CDCl₃, 300 MHz) δ 8.15 (d, J = 7.5 Hz, 1H), 7.90-7.82 (m, 5H), 7.58-7.46 (m, 3H), 3.85 (s, 3H), 3.77 (s, 3H), 3.73 (s, 3H), 3.58 (s, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 172.0, 167.6, 165.2, 133.6, 133.3, 132.8, 131.2, 129.1, 128.6, 126.3, 125.8, 125.5, 124.4, 123.2, 123.0, 113.0, 60.5, 51.9, 51.7, 32.6; IR (KBr) ν 2950 (m), 2841 (m), 1742 (s), 1613 (m), 1582 (m), 1508 (m), 1435 (m), 797 (m), 775 (m); MS (EI, m/z, rel. intensity) 341 (2.3, M⁺), 309 (5.6), 267 (40), 249 (14), 235 (100), 221 (24), 206 (5.1), 189 (16), 178 (7.8), 165 (4.6), 152 (10), 127 (2.0), 113 (1.8), 101 (0.5), 89 (1.1), 76 (1.6), 59 (11), 45 (1.8); HRMS (EI) calcd for
C_{20}H_{20}O_{5} (M^+) : 340.1311; Found: 340.1314.

64\%, yield, white solid, ^1H NMR (CDCl₃, 400 MHz) δ 7.44 (d, J = 7.2 Hz, 2H), 7.36-7.24 (m, 4H), 7.01-6.95 (m, 1H), 6.90-6.83 (m, 1H), 6.75 (d, J = 15.2 Hz, 1H), 3.75 (s, 3H), 3.71 (s, 3H), 3.70 (s, 3H), 3.52 (s, 2H); ^13C NMR (CDCl₃, 100 MHz) δ 172.0, 167.6, 165.2, 136.7, 136.63, 136.60, 128.6, 128.27, 128.23, 126.7, 124.3, 112.8, 60.6, 51.9, 51.7, 32.6; IR (KBr) ν 2950(m), 2850 (m), 1738 (s), 1707 (s), 1605 (m), 1256 (m), 1054 (s), 998 (s), 788 (m), 751 (m), 738 (m), 693 (m); MS (EI, m/z, rel. intensity) 316 (23, M^+), 285 (4.5), 270 (5.5), 256 (5.6), 242 (27), 225 (20), 211 (100), 197 (62), 181 (19), 157 (88), 153 (33), 128 (89), 115 (51), 105 (84), 91 (91), 84 (78), 59 (100), 43 (78); HRMS (EI) calcd for C_{18}H_{20}O_{5} (M^+) : 316.1311; Found: 316.1305.

72\% yield, colorless liquid, ^1H NMR (CDCl₃, 300 MHz) δ 7.31-7.26 (m, 2H), 7.20-7.19 (m, 3H), 6.95 (d, J = 15.6 Hz, 1H), 6.29-6.20 (m, 1H), 3.71 (s, 3H), 3.68 (s, 3H), 3.58 (s, 3H), 3.45 (s, 2H), 2.82-2.77 (m, 2H), 2.60-2.53 (m, 2H); ^13C NMR (CDCl₃, 100 MHz) δ 172.1, 167.8, 165.1, 141.2, 138.9, 128.32, 128.31, 125.9, 122.7, 110.8, 59.9, 51.8, 51.6, 35.0, 34.5, 32.4; IR (KBr) ν 2949 (m), 2850 (m), 1739 (s), 1589 (m), 1435 (m), 1193 (s), 1053 (s), 1015 (s), 801 (s), 736 (s), 700 (s); MS (EI, m/z, rel. intensity) 318 (17, M^+), 286 (5.6), 254 (8.4), 227 (22), 213 (100), 195 (5.9), 173 (9.8), 167 (12), 139 (8.3), 117 (10), 109 (12), 91 (68), 77 (4.8), 65 (10.2), 59 (9.4), 41 (2.9); HRMS (EI) calcd for C_{18}H_{22}O_{5} (M^+) : 318.1467; Found: 318.1469.

49\% yield, colorless liquid, ^1H NMR (CDCl₃, 400 MHz) δ 6.92 (d, J = 16.0 Hz,
1H), 6.28-6.20 (m, 1H), 3.72 (s, 3H), 3.69 (s, 3H), 3.66 (s, 3H), 3.46 (s, 2H),
2.26-2.20 (m, 2H), 1.48-1.45 (m, 2H), 1.30-1.28 (m, 8H), 0.88-0.87 (m, 3H); $^{13}$C
NMR (CDCl$_3$, 100 MHz) $\delta$ 172.2, 167.8, 165.4, 140.3, 122.0, 110.4, 60.0, 51.8, 51.5,
32.8, 32.4, 31.7, 29.1, 29.0, 28.7, 22.5, 14.0; IR (KBr) v 2926 (m), 2855 (m), 1742 (s),
1715 (s), 1640 (m), 1590 (m), 1435 (m), 1194 (m), 1117 (m), 1059 (m), 978 (m), 800
(m); MS (EI, m/z, rel. intensity) 312 (8.4, M$^+$), 281 (5.8), 253 (5.0), 213 (100), 196
(5.7), 177 (4.8), 164 (16), 149 (3.1), 137 (4.0), 123 (8.1), 109 (9.3), 95 (9.1), 79 (6.1),
59 (7.7), 41 (13); HRMS (EI) calcd for C$_{17}$H$_{28}$O$_5$ (M$^+$): 312.1937; Found: 312.1941.
X-Ray Structure of (3E, 5E)-4e (CCDC 932306)

Bond precision: C-C = 0.0026 Å  
Wavelength=0.71073 Å

Cell:  
a=7.5752(9)  b=9.2925(12)  c=11.9191(15)  
alpha=90.060(2)  beta=98.984(2)  gamma=95.356(2)

Temperature: 293 K

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total
R(reflections)= 0.0571( 2472)  wR2(reflections)= 0.1731( 3205)
S = 1.032  Npar= 221
5. Reaction Conditions for Synthesis of Cyclopentadienes

Table S2 Solvent effects

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<th>Entry</th>
<th>Solvent</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Entry</th>
<th>Solvent</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
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<sup>a</sup> Condition: ylide 2c (167.4 mg, 0.4 mmol), PhCOCHN<sub>2</sub> (116.8 mg, 0.8 mmol), Fe(TCP)Cl (1.7 mg, 0.002 mmol), solvent (4.0 mL), RT; <sup>b</sup> Isolated yield.

Table S3 Reaction time

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<th>Entry</th>
<th>t (h)</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Entry</th>
<th>t (h)</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
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<sup>a</sup> Condition: ylide 2c (167.4 mg, 0.4 mmol), PhCOCHN<sub>2</sub> (116.8 mg, 0.8 mmol), Fe(TCP)Cl (1.7 mg, 0.002 mmol), DCE (4.0 mL); <sup>b</sup> Isolated yield.
### Table S4 Loading of diazo phenylethanone

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<th>Entry</th>
<th>Ylide/Diazo</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Entry</th>
<th>Ylide/Diazo</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
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<td>1.0/1.2</td>
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<td>1.0/1.4</td>
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<td>6</td>
<td>1.0/2.5</td>
<td>54</td>
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<sup>a</sup> Condition: ylide 2c (167.4 mg, 0.4 mmol), PhCOCHN₂, Fe(TCP)Cl (1.7 mg, 0.002 mmol), DCE (4.0 mL), 6 h; <sup>b</sup> Isolated yield.

### Table S5 Reaction temperature

<table>
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<th>Entry</th>
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<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Entry</th>
<th>T (°C)</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
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<sup>a</sup> Condition: ylide 2c (167.4 mg, 0.4 mmol), PhCOCHN₂ (81.8 mg, 0.56 mmol), Fe(TCP)Cl (1.7 mg, 0.002 mmol), DCE (4.0 mL), 6 h; <sup>b</sup> Isolated yield; <sup>c</sup> Under the same condition, t = 12 h.
6. General Procedure for Synthesis of Cyclopentadienes

General procedure: To a stirred suspension of ylide 2 (0.4 mmol) in dry DCE (2.0 mL) under N₂ at room temperature was added Fe(TCP)Cl (1.7 mg, 0.002 mmol) and RCOCHN₂ (0.56 mmol) sequentially at 20 °C. (Caution! N₂ Release!) The resulting mixture was stirred at 20 °C for 6 hours. After the reaction was complete, the resulting mixture was concentrated and the residue was purified by chromatography on silica gel to afford the desired products.

65% yield, light yellow solid, ¹H NMR (CDCl₃, 400 MHz) δ 7.58 (d, J = 6.8 Hz, 2H), 7.39-7.29 (m, 3H), 6.93 (s, 1H), 4.04 (s, 3H), 3.78 (s, 3H), 3.70 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 168.2, 164.3, 152.9, 134.3, 128.80, 128.79, 125.5, 119.0, 104.6, 58.6, 50.8, 38.3; IR (KBr) ν 2946 (m), 1697 (s), 1673 (s), 1610 (m), 1456 (m), 1392 (m), 1209 (s), 1079 (s); MS (EI, m/z, rel. intensity) 230 (81, M⁺), 199 (21), 171 (100), 155 (13), 142 (10), 128 (48), 115 (17), 105 (17), 91 (5.5), 77 (16), 57 (4); HRMS (EI) calcd for C₁₄H₁₄O₃ (M⁺): 230.0943; Found: 230.0947.

74% yield, light yellow solid, ¹H NMR (CDCl₃, 300 MHz) δ 7.58 (d, J = 7.5 Hz, 2H), 7.40-7.29 (m, 3H), 6.90 (s, 1H), 4.32 (q, J = 7.1 Hz, 2H), 3.78 (s, 3H), 3.70 (s, 2H), 1.47 (t, J = 6.9 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 167.7, 164.4, 152.7, 134.4, 128.8, 128.76, 125.5, 119.7, 104.8, 67.1, 50.7, 38.1, 15.2; IR (KBr) ν 2983 (m), 2945 (m), 1697 (s), 1674 (s), 1609 (m), 1448 (m), 1386 (m), 1208 (s), 1074 (s); MS (EI, m/z, rel. intensity) 244 (83, M⁺), 213 (17), 185 (38), 157 (77), 128 (100), 115 (18), 108 (12), 102 (21), 91 (5.5), 77 (16); HRMS (EI) calcd for C₁₅H₁₆O₃ (M⁺): 244.1099; Found: 244.1100.
76% yield, light yellow solid, $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.57 (d, $J = 6.9$ Hz, 2H), 7.40-7.30 (m, 3H), 6.89 (s, 1H), 4.35-4.20 (m, 4H), 3.69 (s, 2H), 1.47 (t, $J = 7.0$ Hz, 3H), 1.33 (t, $J = 7.0$ Hz, 3H).

50% yield, light yellow solid, $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.56 (d, $J = 6.9$ Hz, 2H), 7.38-7.26 (m, 3H), 6.87 (s, 1H), 4.29 (q, $J = 7.1$ Hz, 2H), 3.62 (s, 2H), 1.54 (s, 9H), 1.46 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 170.0, 163.8, 151.8, 134.7, 128.8, 128.5, 125.5, 119.8, 106.9, 79.0, 66.8, 38.2, 28.5, 15.2; IR (KBr) $\nu$ 2976 (m), 2928 (m), 1693 (s), 1670 (s), 1610 (m), 1413 (m), 1389 (m), 1168 (s), 1063 (m); MS (EI, m/z, rel. intensity) 286 (30, M$^+$), 244 (26), 230 (48), 213 (24), 184 (55), 157 (74), 128 (100), 115 (17), 108 (26), 91 (9), 77 (20), 57 (36); HRMS (EI) calcd for C$_{18}$H$_{22}$O$_3$ (M$^+$): 286.1569; Found: 286.1565.

40% yield, light yellow liquid, $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.57 (d, $J = 7.5$ Hz, 2H), 7.40-7.28 (m, 3H), 6.90 (s, 1H), 5.96-5.82 (m, 1H), 5.13 (m, 2H), 4.34-4.22 (m, 4H), 3.68 (s, 2H), 2.47 (q, $J = 6.8$ Hz, 2H), 1.47 (t, $J = 7.0$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 167.8, 164.0, 152.6, 134.7, 134.4, 128.8, 128.7, 125.5, 119.7, 116.8, 104.9, 67.0, 62.5, 37.9, 33.4, 15.2; IR (KBr) $\nu$ 2979 (m), 2927 (m), 1698 (s), 1672 (s), 1609 (m), 1205 (s), 1071 (s); MS (EI, m/z, rel. intensity) 284 (30, M$^+$), 255 (5.6), 230 (10), 213 (30), 199 (15), 186 (50), 157 (100), 128 (85), 115 (20), 108 (63), 102 (21), 91 (11), 77 (23), 55 (46); HRMS (EI) calcd for C$_{18}$H$_{20}$O$_3$ (M$^+$): 284.1412; Found: 284.1413.
45% yield, light yellow solid, $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.49 (d, $J = 8.4$ Hz, 2H), 7.42 (d, $J = 8.8$ Hz, 2H), 6.89 (s, 1H), 4.33-4.21 (m, 4H), 3.84 (s, 3H), 3.64 (s, 2H), 1.46 (t, $J = 7.0$ Hz, 3H), 1.32 (t, $J = 7.0$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 168.2, 164.1, 160.1, 152.5, 127.4, 127.0, 117.7, 114.1, 104.0, 67.0, 59.2, 55.3, 38.0, 15.2, 14.6; IR (neat) v 2926 (m), 2853 (m), 1667 (s), 1605 (s), 1506 (m), 1425 (m), 1254 (s), 1207 (s), 1025 (s), 811 (m), 738 (m); MS (EI, m/z, rel. intensity) 288 (43, M$^+$), 259 (4.8), 243 (11), 231 (4.3), 215 (36), 203 (5.0), 187 (70), 172 (11), 158 (14), 144 (21), 128 (27), 115 (100), 102 (13), 89 (42), 77 (29), 63 (26), 55 (17), 43 (19); HRMS (EI) calcd for C$_{17}$H$_{20}$O$_4$ (M$^+$): 288.1362; Found: 288.1366.

57% yield, light yellow solid, $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.57-7.52 (m, 2H), 7.08-7.03 (m, 2H), 6.82 (s, 1H), 4.34-4.20 (m, 4H), 3.65 (s, 2H), 1.46 (t, $J = 7.0$ Hz, 3H), 1.32 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 167.6, 164.0 (d, $J = 14.8$ Hz, 1C), 161.6, 151.2, 130.8 (d, $J = 4.0$ Hz, 1C), 127.3 (d, $J = 7.5$ Hz, 1C), 119.6,
115.8 (d, \(J = 22.6\) Hz, 1C), 105.0, 67.0, 59.2, 38.2, 15.1, 14.5; \(^{19}\)F NMR (CDCl\(_3\), 376 MHz) \(\delta\) -112.2 – -112.3 (m, 1F); IR (neat) \(\nu\) 2982 (m), 2926 (m), 1691 (s), 1610 (s), 1503 (s), 1207 (s), 1097 (s), 823 (s), 736 (s); MS (EI, m/z, rel. intensity) 337 (22, M\(^+\)), 308 (8.0), 276 (48), 248 (4.7), 231 (17), 203 (41), 175 (100), 146 (84), 133 (19), 120 (24), 101 (8.2), 83 (13), 57 (7.6), 43 (13); HRMS (EI) calcd for C\(_{16}\)H\(_{17}\)FO\(_3\) (M\(^+\)): 276.1162; Found: 276.1163.

![Chemical structure 5i](image)

48% yield, light yellow solid, \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.49 (d, \(J = 8.4\) Hz, 2H), 7.33 (d, \(J = 8.8\) Hz, 2H), 6.87 (s, 1H), 4.33-4.21 (m, 4H), 3.64 (s, 2H), 1.46 (t, \(J = 7.2\) Hz, 3H), 1.32 (t, \(J = 7.0\) Hz, 3H); \(^1\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 167.4, 163.9, 150.9, 134.4, 133.0, 129.0, 126.7, 120.3, 105.4, 67.1, 59.3, 38.1, 15.2, 15.0; IR (KBr) \(\nu\) 2979 (m), 2929 (m), 1662 (s), 1610 (m), 1434 (m), 1206 (s), 1103 (m), 813 (m); MS (EI, m/z, rel. intensity) 292 (90, M\(^+\)), 264 (8.1), 247 (25), 220 (60), 191 (100), 155 (25), 127 (46), 115 (13), 101 (12), 75 (10), 43 (10); HRMS (EI) calcd for C\(_{16}\)H\(_{17}\)ClO\(_3\) (M\(^+\)): 292.0866; Found: 292.0867.

![Chemical structure 5j](image)

48% yield, light yellow solid, \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.49 (d, \(J = 8.4\) Hz, 2H), 7.42 (d, \(J = 8.8\) Hz, 2H), 6.89 (s, 1H), 4.33-4.21 (m, 4H), 3.64 (s, 2H), 1.46 (t, \(J = 7.0\) Hz, 3H), 1.32 (t, \(J = 7.0\) Hz, 3H); \(^1\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 167.4, 163.9, 150.9, 133.3, 131.9, 126.9, 122.6, 120.4, 105.5, 67.1, 59.3, 38.0, 15.1, 14.5; IR (neat) \(\nu\) 2982 (m), 2854 (m), 1689 (s), 1664 (s), 1610 (s), 1206 (s), 1069 (s), 810 (s), 736 (s); MS (EI, m/z, rel. intensity) 337 (22, M\(^+\)), 308 (8.0), 291 (21), 264 (92), 235 (100), 155 (42), 128 (79), 115 (27), 101 (22), 75 (20), 43 (15); HRMS (EI) calcd for C\(_{16}\)H\(_{17}\)BrO\(_3\) (M\(^-\)): 336.0361; Found: 336.0358.
70% yield, light yellow solid, $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.70 (s, 1H), 7.49-7.40 (m, 2H), 7.26-7.20 (m, 1H), 6.90 (s, 1H), 4.34-4.20 (m, 4H), 3.64 (s, 2H), 1.46 (t, $J$ = 6.9 Hz, 3H), 1.33 (t, $J$ = 7.0 Hz, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 167.2, 163.8, 150.5, 136.5, 131.4, 130.3, 128.4, 124.0, 123.0, 121.1, 105.8, 67.1, 59.3, 38.0, 15.1, 14.5; IR (KBr) $\nu$ 2982 (m), 2929 (m), 1693 (s), 1610 (s), 1561 (m), 1209 (s), 1070 (s), 737 (s); MS (EI, m/z, rel. intensity) 338 (19, M$^+$), 293 (9.1), 264(34), 235 (33), 153 (92), 127 (31), 110 (52), 97 (95), 81 (61), 57 (100), 43 (97); HRMS (EI) calcd for C$_{16}$H$_{17}$BrO$_3$ (M$^+$): 336.0361; Found: 336.0366.

46% yield, light yellow solid, $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.46 (d, $J$ = 8.2 Hz, 2H), 7.35 (t, $J$ = 8.2 Hz, 2H), 7.29-7.24 (m, 1H), 7.00 (d, $J$ = 16.2 Hz, 1H), 6.90 (d, $J$ = 15.9 Hz, 1H), 6.52 (s, 1H), 4.28-4.20 (m, 4H), 3.54 (s, 2H), 1.44 (t, $J$ = 7.0 Hz, 3H), 1.32 (t, $J$ = 6.9 Hz, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 167.7, 164.0, 151.8, 136.5, 131.7, 128.8, 128.2, 126.6, 123.8, 123.3, 104.5, 67.0, 59.2, 36.5, 15.1, 14.6; IR (KBr) $\nu$ 2986 (m), 2939 (m), 1669(s), 1693 (s), 1595 (s), 1524 (m), 1210 (s), 1147 (m), 1069 (s); MS (EI, m/z, rel. intensity) 284 (93, M$^+$), 239 (30), 210 (52), 183 (80), 165 (100), 153 (78), 141 (37), 128 (35), 115 (26), 102 (9.0), 91 (12), 77 (16), 55(19); HRMS (EI) calcd for C$_{18}$H$_{20}$O$_3$ (M$^+$): 284.1412; Found: 284.1415.

70% yield, light yellow solid, $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.42 (s, 2H), 6.75 (s, 1H), 6.55 (d, $J$ = 3.0 Hz, 1H), 6.46-6.44 (m, 1H), 4.32-4.19 (m, 4H), 3.60 (s, 2H), 1.45 (t, $J$ = 6.9 Hz, 3H), 1.32 (t, $J$ = 6.9 Hz, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 167.8, 164.0, 150.9, 142.9, 141.5, 118.1, 111.9, 108.7, 103.7, 67.0, 59.2, 36.9, 15.1, 14.5; IR
(KBr) ν 2980 (m), 2934 (m), 1697(s), 1620 (m), 1577 (s), 1523 (m), 1217 (s), 1199 (m), 1068 (s); MS (EI, m/z, rel. intensity) 248 (48, M+), 175 (47), 147 (100), 118 (16), 91 (19), 77 (5.4), 65 (11), 55 (3.7); HRMS (EI) calcd for C_{14}H_{16}O_{4}(M^+): 248.1049; Found: 248.1052.
7. Procedure for Chemical Transformation

To a solution of 5c (103.3 mg, 0.4 mmol) in CHCl₃ (8.0 mL) was added aq. HCl (8.0 mL, 2.0 M in H₂O) at room temperature. After stirred at the same temperature for 24 hours, the aqueous layer was extracted with CHCl₃ (3 × 10 mL). The combined organic layer was dried over MgSO₄, filtered and concentrated. The residue was purified by chromatography on silica gel to afford the desired product 6 (85.6 mg, 94% yield).

¹H NMR (CDCl₃, 400 MHz) δ 7.69-7.67 (m, 2H), 7.53-7.45 (m, 3H), 6.53 (t, J = 1.8 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.63 (dd, J = 2.2, 10.5Hz, 1H), 3.55 (ddd, J = 1.9, 2.9, 18.0 1H), 3.25 (ddd, J = 1.7, 3.3, 18.2 Hz, 1H), 1.32 (t, J = 7.0 Hz, 3H).
8. General Procedure for Deuterium Experiment

**Synthesis of d3-MDA**

![Chemical Reaction]

To a mixture of MsN₃ (9.1 g, 75 mmol), NaOAc (492 mg, 6 mmol) in CH₃CN (60 mL) was added CD₃OD (2.7 mL, 60 mmol) under N₂. The resulting mixture was heated to 60 °C, and then diketene (9.2 mL, 120 mmol) in CH₃CN (10 mL) was added dropwise in 7 hours. After refluxed for 20 hours, the reaction system was cooled to room temperature and diluted with brine (50 mL). The aqueous layer was extracted with Et₂O (3 × 50 mL), and the combined organic layers were dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The residue was subjected to the next step without further purification.

To a solution of upper products in Et₂O (200 mL) was added KOH (150 mL, 7 wt% in water, 210 mmol) at 0 °C, and then the reaction was warmed up to room temperature. After the reaction was complete, the organic layer was separated and the aqueous layer was extracted with Et₂O (3 × 50 mL). The combined organic layers were dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by distillation under vacuum to afford d₃-MDA as a light yellow liquid (2.2 g, 43% for two steps).

¹H NMR (CDCl₃, 400 MHz) δ 4.76 (brs, 1H).

**Deuterium Experiment**

![Chemical Reaction]

To a stirred suspension of phosphorus ylide 2a (195 mg, 0.5 mmol) in dry CH₃CN (2.0 mL) under N₂ at room temperature was added Fe(TCP)Cl (1.7 mg, 0.002 mmol), d₃-MDA (50 μL, 0.6 mmol) and CH₂CN (1.0 mL) were added to the system
sequentially (Caution! N₂ Release!). Ten minutes later, o-NO₂C₆H₄CHO (60.4 mg, 0.4 mmol) and CH₃CN (1.0 mL) were added and the resulting mixture was stirred at room temperature for 6 hours. After the reaction was complete, the resulting mixture was filtered rapidly through a funnel with a thin layer of silica gel and eluted with CH₂Cl₂. The filtrate was concentrated and the residue was purified by chromatography on silica gel to afford the desired products (3E, 5E)-4c as a light yellow solid (123.8 mg, 92% yield).

![Chemical Structure](image)

92% yield, light yellow solid, ¹H NMR (CDCl₃, 400 MHz) δ 8.01 (d, J = 8.4 Hz, 1 H), 7.81-7.71 (m, 2H), 7.63 (t, J = 7.0 Hz, 1H), 7.50-7.43 (m, 2H), 3.83 (s, 3H), 3.77 (s, 2.4 H), 3.72 (s, 0.6 H), 3.56 (s, 2H).
References:

9. NMR Spectra of the Compounds

\[ \text{\(^1\text{H NMR (400 MHz in CDCl}_3\))} \]
$^{13}$C NMR (100 M Hz in CDCl$_3$)
(2E, 4E)-9a

$^1$H NMR (400 MHz in CDCl$_3$)
$^{13}$C NMR (100 MHz in CDCl$_3$)
\[ (2E, 4Z)-9a \]

\[ ^1H \text{NMR (400 MHz in CDCl}_3) \]
(3E, 5E)-4a

$^1$H NMR (400 MHz in CDCl$_3$)
(3E, 5E)-4a

$^{13}$C NMR (100 M Hz in CDCl$_3$)
(3E, 5Z)-4a

\[^1^H\text{NMR}\ (400\text{ M Hz in CDCl}_3)\]

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$^{13}$C NMR (100 M Hz in CDCl$_3$)
(3E, 5E)-4b

$^1$H NMR (400 MHz in CDCl$_3$)
$^{13}$C NMR (100 M Hz in CDCl$_3$)
(3E,5E)-4c

$^1$H NMR (400 M Hz in CDCl$_3$)
(3E,5E)-4d

$^1$H NMR (400 MHz in CDCl$_3$)
(3E, 5E)4d

$^{13}$C NMR (100 M Hz in CDCl$_3$)
(3E,5E)-4e

$^1$H NMR (400 MHz in CDCl$_3$)
\((3E, 5E)-4e\)

\[^{13}C\text{ NMR (100 M Hz in CDCl}_3\text{)}\]
(3E, 5E)-4f

$^1$H NMR (400 MHz in CDCl$_3$)
(3E, 5E)-4f

$^{13}$C NMR (100 MHz in CDCl$_3$)
(3E, 5E)-4g

$^1$H NMR (400 M Hz in CDCl$_3$)
(3E, 5E)-4g

$^{13}$C NMR (100 M Hz in CDCl$_3$)
(3E, 5E)-4h

$^1$H NMR (400 MHz in CDCl$_3$)
(3E, 5E)-4h

$^{13}$C NMR (100 M Hz in CDCl$_3$)
(3E, 5E)-4i

$^1$H NMR (400 MHz in CDCl$_3$)
$^{13}$C NMR (100 M Hz in CDCl$_3$)
(3E, 5E)-4j

$^1$H NMR (400 MHz in CDCl$_3$)
$^{13}\text{C NMR (100 M Hz in CDCl}_3\text{)}$
\((3E, 5E)-4k\)

$^1$H NMR (300 MHz in CDCl$_3$)
(3E, 5E)-4k

$^{13}$C NMR (100 M Hz in CDCl$_3$)
(3E, 5E)-41

$^1$H NMR (300 M Hz in CDCl$_3$)
(3E, 5E)-41

$^{13}$C NMR (100 MHz in CDCl$_3$)
(3E, 5E)-4m

$^1$H NMR (400 M Hz in CDCl₃)
(3E, 5E)-4m

$^{13}$C NMR (100 MHz in CDCl$_3$)
(3E, 5E)-4n

$^1$H NMR (300 M Hz in CDCl$_3$)
(3E, 5E)-4n

$^{13}$C NMR (100 M Hz in CDCl$_3$)
(3E, 5E)-4o

$^1$H NMR (400 M Hz in CDCl$_3$)
(3E, 5E)-4o

$^{13}$C NMR (100 M Hz in CDCl$_3$)
$^1$H NMR (400 MHz in CDCl$_3$)
$^{13}$C NMR (100 MHz in CDCl$_3$)
$^1$H NMR (300 M Hz in CDCl$_3$)
\[ ^{13}\text{C NMR (100 M Hz in CDCl}_3) \]
$^1$H NMR (300 MHz in CDCl$_3$)
$^1$H NMR (300 M Hz in CDCl$_3$)
$^1$C NMR (100 MHz in CDCl$_3$)
$^1$H NMR (300 M Hz in CDCl$_3$)
$^{13}$C NMR (75 M Hz in CDCl$_3$)
$^1$H NMR (400 MHz in CDCl$_3$)
$^{13}$C NMR (100 M Hz in CDCl$_3$)
$^1$H NMR (300 M Hz in CDCl$_3$)
$^{13}$C NMR (75 MHz in CDCl$_3$)
$^1$H NMR (300 MHz in CDCl$_3$)
$^{13}$C NMR (100 M Hz in CDCl$_3$)
$^{19}$F NMR (376 MHz in CDCl$_3$)
\[ ^1H \text{NMR (400 M Hz in CDCl}_3 \text{)} \]
$^{13}$C NMR (100 M Hz in CDCl$_3$)
$^1$H NMR (400 MHz in CDCl$_3$)
$^{13}$C NMR (100 MHz in CDCl$_3$)
$^1$H NMR (300 M Hz in CDCl$_3$)
$^{13}$C NMR (75 M Hz in CDCl$_3$)
$^1$H NMR (300 M Hz in CDCl$_3$)
$^{13}$C NMR (75 M Hz in CDCl$_3$)
$^1$H NMR (300 M Hz in CDCl$_3$)
$^{13}$C NMR (75 M Hz in CDCl$_3$)
$^1$H NMR (400 MHz in CDCl$_3$)
$^1$H NMR (400 MHz in CDCl$_3$)
$^1$H NMR (300 MHz in CDCl$_3$)