Supporting information

DBU-catalyzed cyclization of electron-deficient 1,3-conjugated enynes with 2-aminomalonates: a facile access to highly substituted 2,3-dihydro-1H-pyrroles

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The control experiments about the reactivity of $E$- and $Z$-isomers:

The control experiment indicated $Z$-isomer is more reactive than the $E$-isomer.

Typical procedure for the synthesis of 2-pyrroline 3a (Table 1, entry 3):

1. 2,2-Diethyl 4-methyl 1-acetyl-5-benzyl-3-phenyl-1$H$-pyrrole-2,2,4(3$H$)-tricarboxylate.

Under Ar, DBU (15.2 mg, 0.1 mmol) was added to a mixture of enyne 1a ($E/Z = 1.1/1$, 131.0 mg, 0.5 mmol) and 2-acetamidomalonate 2a (163.0 mg, 0.75 mmol) in dry DMF (2.5 mL) at 40 °C. The reaction was stirred at this temperature till the complete consumption of 2a which was determined by TLC analysis. After cooling down to room temperature, H$_2$O (5 mL) was added to the reaction mixture which was then extracted by diethyl ether (3 × 10 mL). The combined organic phase was washed by water and saturated aqueous NaCl solution and dried over MgSO$_4$. After filtration and concentration, the residue was purified by column chromatography on silica gel (PE : EA = 5 : 1) to give 3a in 90% (215.1 mg) yield as a white solid. m.p.: 87 ~ 88 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.35 ~ 7.15$ (m, 10 H), 4.91 (d, $J = 15.9$ Hz, 1 H), 4.87
(s, 1 H), 4.70 (d, J = 15.9 Hz, 1 H), 4.38 ~ 4.16 (m, 2 H), 3.60 ~ 3.50 (m, 1 H), 3.45 (s, 3 H), 3.43 ~ 3.33 (m, 1 H), 2.06 (s, 3 H), 1.26 (t, J = 7.2 Hz, 3 H), 0.85 (m, J = 7.2 Hz, 3 H). $^{13}$C NMR (75.5 MHz, CDCl$_3$): 169.55, 167.49, 164.75, 164.25, 153.73, 137.21, 136.63, 128.40 (2C), 127.78(2C), 127.62, 126.34, 112.41, 78.44, 62.52, 61.67, 54.11, 51.07, 32.09, 24.62, 13.65, 13.11 ppm. IR (neat): ν (cm$^{-1}$) 3444, 3029, 1759, 1687, 1625, 1307, 1232, 1047, 1012, 699. HRMS calcd for C$_{27}$H$_{29}$NO$_7$: 479.1944, found: 479.1959. MS (70 eV): m/z (%): 479 (M$^+$, 0.60), 91 (100).

2. **2,2-Diethyl 4-methyl 1-acetyl-5-(naphthalen-1-ylmethyl)-3-phenyl-1H-pyrrole-2,2,4(3H)-tricarboxylate.**

![Chemical structure](image)

A mixture of 1b ($E/Z = 1.5/1$, 156.0 mg, 0.5 mmol), 2a (163.0 mg, 0.75 mmol), and DBU (15.2 mg, 0.10 mmol) in 2.5 mL of DMF was stirred at 40 °C for 41 h to afford 3b in the yield of 72% (190.4 mg). Colorless oil, $^1$H NMR (300 MHz, CDCl$_3$): δ = 8.08 (d, J = 8.4 Hz, 1 H), 7.91 (d, J = 7.5 Hz, 1 H), 7.84 ~ 7.77 (m, 1 H), 7.64 ~ 7.51 (m, 3 H), 7.50 ~ 7.42 (m, 1 H), 7.36 ~ 7.26 (m, 5 H), 5.22 (d, J = 15.6 Hz, 1 H), 5.18 (d, J = 15.6 Hz, 1 H), 4.90 (s, 1 H), 4.47 ~ 4.27 (m, 2 H), 3.63 ~ 3.40 (m, 2 H), 3.44 (s, 3 H), 2.02 (s, 3 H), 1.38 (t, J = 7.2 Hz, 3 H), 0.93 (t, J = 7.2 Hz, 3 H). $^{13}$C NMR (75.5 MHz, CDCl$_3$): 169.49, 167.77, 164.98, 164.33, 153.05, 137.67, 133.77, 132.60, 131.44, 128.87, 127.99, 127.77, 127.50, 126.48, 125.88, 125.63, 124.11, 122.72, 113.16, 78.32, 62.67, 61.73, 53.87, 51.29, 30.02, 24.11, 13.98, 13.39 ppm. IR (neat): ν (cm$^{-1}$) 3488, 2993, 1749, 1706, 1664, 1630, 1390, 1335 1226, 1059, 1018, 805, 698. HRMS calcd for C$_{31}$H$_{31}$NO$_7$: 529.2101, found: 529.2094. MS (70 eV): m/z (%): 529 (M$^+$, 0.18), 141 (100).
3. 2,2-Diethyl 4-methyl 5-(4-methoxybenzyl)-1-acetyl-3-phenyl-1H-pyrrole-2,2,4(3H)-tricarboxylate

![Chemical structure of 3c]

A mixture of 1c (E/Z = 1.2/1, 146.0 mg, 0.5 mmol), 2a (163.0 mg, 0.75 mmol), and DBU (15.2 mg, 0.10 mmol) in 2.5 mL of DMF was stirred at 40 °C for 29 h to afford 3c in the yield of 70% (178.2 mg). Yellow oil, \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.30 \sim 7.10\) (m, 7 H), 6.86 (dd, \(J = 2.1, 6.6\) Hz, 2 H), 4.84 (s, 1 H), 4.81 (d, \(J = 15.6\) Hz, 1 H), 4.62 (d, \(J = 15.6\) Hz, 1 H), 3.78 (s, 3 H), 3.57 \sim 3.45 (m, 1 H), 3.48 (s, 3 H), 3.43 \sim 3.35 (m, 1 H), 2.09 (s, 3 H), 1.28 (t, \(J = 7.2\) Hz, 3 H), 0.86 (t, \(J = 7.2\) Hz, 3 H). \(^1^3\)C NMR (75.5 MHz, CDCl\(_3\)): 169.75, 167.67, 164.94, 164.42, 158.20, 154.26, 137.36, 128.92, 128.67, 127.91, 127.73, 113.99, 112.36, 78.58, 62.67, 61.82, 55.12, 54.22, 51.22, 31.37, 24.74, 13.78, 13.25 ppm. IR (neat): \(\nu\) (cm\(^{-1}\)) 2984, 2953, 1746, 1707, 1620, 1511, 1369, 1223, 1133, 1019, 818, 700. HRMS calcd for C\(_{28}\)H\(_{31}\)NO\(_8\): 509.2050, found: 509.2055. MS (70 eV): m/z (%): 509 (M\(^+\), 0.63), 121 (100).

4. 2,2-Diethyl 4-methyl 5-(4-nitrobenzyl)-1-acetyl-3-phenyl-1H-pyrrole-2,2,4(3H)-tricarboxylate

![Chemical structure of 3d]

A mixture of 1d (E/Z = 1.3/1, 153.6 mg, 0.5 mmol), 2a (163.0 mg, 0.75 mmol), and DBU (15.2 mg, 0.10 mmol) in 2.5 mL of DMF was stirred at 40 °C for 1 h to
afford 3d in the yield of 65% (170.3 mg). Yellow solid, m.p.: 134 ~ 135 °C. 1H NMR (300 MHz, CDCl3): \( \delta = 8.16 \text{ (d, } J = 8.7 \text{ Hz, 2 H)}, 7.47 \text{ (d, } J = 8.7 \text{ Hz, 2 H)},
7.30 \sim 7.10 \text{ (m, 5 H)}, 4.99 \text{ (d, } J = 15.6 \text{ Hz, 1 H)}, 4.94 \text{ (s, 1 H)}, 4.83 \text{ (d, } J = 15.6 \text{ Hz, 1 H)},
4.40 \sim 4.26 \text{ (m, 2 H)}, 3.58 \sim 3.50 \text{ (m, 1 H)}, 3.48 \text{ (s, 3 H)}, 3.47 \sim 3.37 \text{ (m, 1 H)},
1.92 \text{ (s, 3 H)}, 1.31 \text{ (t, } J = 7.2 \text{ Hz, 3 H)}, 0.86 \text{ (t, } J = 7.2 \text{ Hz, 3 H}). 13C NMR
(75.5 MHz, CDCl3): 170.20, 167.89, 164.80, 164.64, 153.87, 146.65, 145.39,
136.82, 129.11, 128.16, 123.63, 112.67, 79.09, 63.28, 62.49, 55.38, 51.51, 32.90,
25.04, 13.92, 13.32 ppm. IR (neat): \( v \text{ (cm}^{-1}) \) 2987, 2955, 1745, 1701, 1679,
1515, 1346, 1306, 1233, 1048, 1003, 739, 698. HRMS calcd for C27H28N2O9: 524.1795,
found: 524.1796. MS (70 eV): m/z (%): 524 (M+, 0.79), 409 (100).

5. 2,2-Diethyl 4-methyl 1-acetyl-5-benzyl-3-(4-methoxyphenyl)-1H-pyrrole-2,2,4
(3H)-tricarboxylate.

A mixture of 1e \( (E/Z = 1.3/1, 146.0 \text{ mg, 0.5 mmol}), 2a \) (163.0 mg, 0.75 mmol),
and DBU (15.2 mg, 0.10 mmol) in 2.5 mL of DMF was stirred at 40 °C for 23 h to
afford 3e in the yield of 64% (162.9 mg); White solid, m.p.:105 ~ 106 °C. 1H NMR (300 MHz, CDCl3): \( \delta = 7.36 \sim 7.13 \text{ (m, 7 H)}, 6.81 \text{ (dd, } J = 1.5, 7.5 \text{ Hz, 2 H)},
4.87 \text{ (d, } J = 15.9 \text{ Hz, 1 H)}, 4.82 \text{ (s, 1 H)}, 4.69 \text{ (d, } J = 15.9 \text{ Hz, 1 H)}, 4.36 \sim 4.19 \text{ (m,}
2 H), 3.77 \text{ (s, 3 H)}, 3.64 \sim 3.55 \text{ (m, 1 H)}, 3.58 \sim 3.43 \text{ (m, 4 H)}, 2.06 \text{ (s, 3 H)}, 1.27
(t, } J = 7.2 \text{ Hz, 3 H)}, 0.92 \text{ (t, } J = 7.2 \text{ Hz, 3 H}). 13C NMR (75.5 MHz, CDCl3):
169.86, 167.78, 165.07, 164.56, 159.18, 153.67, 136.91, 129.32, 128.59, 128.00,
126.52, 113.36, 112.92, 78.65, 62.70, 61.93, 55.17, 53.86, 51.34, 32.34, 24.86,
13.85, 13.41 ppm. IR (neat): \( v \text{ (cm}^{-1}) \) 2957, 2846, 2043, 1758, 1686, 1514, 1368,
1284, 1232, 1052, 1013, 854, 731, 697. HRMS calcd for C28H31NO8: 509.2050,
found: 509.2069. MS (70 eV): m/z (%): 509 (M⁺, 1.29), 91 (100).

6. 2,2-Diethyl 4-methyl 1-acetyl-5-benzyl-3-(4-fluorophenyl)-1H-pyrrole-2,2,4 (3H)-tricarboxylate.

A mixture of 1f (E/Z = 1.2/1, 140.0 mg, 0.5 mmol), 2a (163.0 mg, 0.75 mmol), and DBU (15.2 mg, 0.10 mmol) in 2.5 mL of DMF was stirred at 40 °C for 4.5 h to afford 3f in the yield of 89% (221.0 mg). White solid; m.p.: 101 ~ 102 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.36 ~ 7.20 (m, 7 H), 6.98 (t, J = 8.4 Hz, 2 H), 4.89 (d, J = 15.9 Hz, 1 H), 4.84 (s, 1 H), 4.65 (d, J = 15.9 Hz, 1 H), 4.37 ~ 4.19 (m, 2 H), 3.65 ~ 3.59 (m, 1 H), 3.58 ~ 3.44 (m, 2 H), 2.08 (s, 3 H), 1.27 (t, J = 7.2 Hz, 3 H), 0.92 (t, J = 7.2 Hz, 3 H). ¹³C NMR (75.5 MHz, CDCl₃): 169.77, 167.59, 164.86, 164.41, 162.34 (d, J_F-C = 246.9 Hz), 154.08, 136.69, 133.20 (d, J_F-C = 3.0 Hz), 128.65, 127.93, 126.61, 114.91 (d, J_F-C = 21.1 Hz), 112.45, 78.47, 62.82, 62.02, 53.55, 51.37, 32.29, 24.85, 13.84, 13.40 ppm. IR (neat): ν (cm⁻¹) 3067, 2983, 1756, 1706, 1672, 1506, 1380, 1227, 1059, 1018, 1012, 861, 733, 698. HRMS calcd for C₂₇H₂₈NO₇F: 497.1850, found: 497.1856. MS (70 eV): m/z (%): 497 (M⁺, 0.27), 91 (100).

7. 2,2-Diethyl 3,4-dimethyl 1-acetyl-5-benzyl-1H-pyrrole-2,2,3,4(3H)-tetracarboxylate.
A mixture of 1g ($E/Z = 3.2/1$, 73.2 mg, 0.3 mmol), 2a (97.7 mg, 0.45 mmol), and DBU (9.1 mg, 0.06 mmol) in 2.5 mL of DMF was stirred at 40 °C for 3 h to afford 3g in the yield of 81% (112.0 mg). Yellow oil, $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.35 \sim 7.21$ (m, 5 H), 4.68 (s, 2 H), 4.44 (s, 1 H), 4.34 $\sim$ 4.25 (m, 2 H), 4.23 $\sim$ 4.15 (m, 2 H), 3.73 (s, 3 H), 3.68 (s, 3 H), 2.16 (s, 3 H), 1.29 (t, $J = 7.2$ Hz, 3 H), 1.27 (t, $J = 7.2$ Hz, 3 H). $^{13}$C NMR (75.5 MHz, CDCl$_3$): 169.58, 168.85, 166.93, 164.86, 164.41, 153.45, 135.74, 128.89, 127.62, 126.74, 110.04, 76.07, 63.08, 62.79, 53.07, 52.70, 51.64, 32.26, 24.46, 13.85, 13.72 ppm. IR (neat): $v$ (cm$^{-1}$) 2955, 2850, 1751, 1685, 1625, 1438, 12 23, 1199, 1017, 733, 698. HRMS calcd for C$_{23}$H$_{27}$NO$_9$: 461.1686, found: 461.1689. MS (70 eV): m/z (%): 461 (M$^+$, 1.96), 91 (100).

8. 2,2-Diethyl 4-methyl 1-acetyl-5-benzyl-3-methyl-1$^H$-pyrrole-2,2,4(3$^H$)-tricarboxylate.

A mixture of 1h ($E$, 100.0 mg, 0.5 mmol), 2a (163.0 mg, 0.75 mmol), and DBU (15.2 mg, 0.10 mmol) in 2.5 mL of DMF was stirred at 40 °C for 1.5 h to afford 3h in the yield of 49% (102.2 mg). Yellow oil; $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.31 \sim 7.24$ (m, 2 H), 7.21 $\sim$ 7.17 (m, 3 H), 4.59 (s, 2 H), 4.28 $\sim$ 4.16 (m, 4 H), 3.69 (s, 3 H), 3.62 (q, $J = 6.9$ Hz, 1 H), 2.09 (s, 3 H), 1.32 $\sim$1.18 (m, 9 H). $^{13}$C NMR (75.5 MHz, CDCl$_3$): 169.41, 167.70, 164.95, 164.93, 151.13, 136.39, 128.48, 127.53, 126.34, 115.23, 77.06, 62.24, 61.80, 51.13, 43.15, 31.94, 24.48, 16.68, 13.82, 13.69 ppm. IR (neat): $v$ (cm$^{-1}$) 2983, 2953, 1745, 1707, 1679, 1619, 1371, 1222, 1097, 1031, 729, 698. HRMS calcd for C$_{22}$H$_{27}$NO$_7$: 417.1788, found: 417.1806. MS (70 eV): m/z (%): 417 (M$^+$, 1.96), 91 (100).

9. Diethyl 1,4-diacetyl-5-benzyl-3-phenyl-1$^H$-pyrrole-2,2(3$^H$)-dicarboxylate.
A solution of 1i (E, 123.0 mg, 0.5 mmol) in 1.5 mL of DMF was slowly added to a solution of 2a (163.0 mg, 0.75 mmol) and DBU (15.2 mg, 0.10 mmol) in 1.0 mL of DMF via syringe pump over 2 h at 40 °C. After finishing addition, the mixture was then stirred for another 26 h. After the routine work-up, 2-pyrroline 3i was obtained in the yield of 70% (163.0 mg). White solid, m.p.: 111 ~ 112 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.36 \sim 7.12\) (m, 10 H), 4.89 (s, 1 H), 4.87 (d, \(J = 15.6\) Hz, 1 H), 4.64 (d, \(J = 15.6\) Hz, 1 H), 4.39 ~ 4.29 (m, 1 H), 4.28 ~ 4.17 (m, 1 H), 3.62 ~ 3.50 (m, 1 H), 3.43 ~ 3.32 (m, 1 H), 2.07 (s, 3 H), 1.88 (s, 3 H), 1.25 (t, \(J = 7.2\) Hz, 3 H), 0.85 (t, \(J = 7.2\) Hz, 3 H). \(^13\)C NMR (75.5 MHz, CDCl\(_3\)): 195.48, 169.93, 167.51, 164.16, 152.82, 136.70, 136.63, 128.40, 128.26, 128.19, 127.84, 126.35, 119.96, 78.67, 62.63, 61.76, 54.88, 32.20, 29.92, 24.82, 13.63, 13.13 ppm. IR (neat): \(v\) (cm\(^{-1}\)) 3463, 2986, 1759, 1740, 1669, 1574, 1378, 1222, 1063, 1026, 744, 700. HRMS calcld for C\(_{27}\)H\(_{29}\)NO\(_6\): 463.1995, found: 463.2015. MS (70 eV): m/z (%): 463 (M\(^+\), 3.80), 260 (100) ppm.

10. Diethyl 1,4-diacetyl-5-(4-methoxybenzyl)-3-phenyl-1\(H\)-pyrrole-2,2(3\(H\))-dicarboxylate.

According to the procedure of synthesis of 3i, the reaction of 2a (97.7 mg, 0.45 mmol), 1\(j\) (E, 82.8 mg, 0.3 mmol) in DMF under the catalysis of DBU (9.1 mg,
0.06 mmol) at 40 °C for 70 h affords 3j in the yield of 61% (90.0 mg). Colorless oil, \( ^1 \)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.31 \) (bs, 4 H), 7.21 (d, \( J = 7.6 \) Hz, 3 H), 6.87 (d, \( J = 8.0 \) Hz, 2 H), 4.89 (s, 1 H), 4.79 (d, \( J = 15.6 \) Hz, 1 H), 4.59 (d, \( J = 15.6 \) Hz, 1 H), 4.40 ~ 4.20 (m, 2 H), 3.79 (s, 3 H), 3.61 ~ 3.53 (m, 1 H) 3.46 ~ 3.37 (m, 1 H), 2.13 (s, 3 H), 1.90 (s, 3 H), 1.29 (t, \( J = 6.8 \) Hz, 3 H), 0.88 (t, \( J = 6.8 \) Hz, 3 H). \( ^{13} \)C NMR (100 MHz, CDCl\(_3\)): 195.64, 170.08, 167.70, 164.32, 158.20, 153.36, 136.85, 128.98, 128.64, 128.40, 128.31, 119.90, 113.98, 78.79, 62.79, 61.90, 55.14, 54.96, 31.48, 30.09, 24.96, 13.77, 13.28 ppm. IR (neat): \( \nu \) (cm\(^{-1}\)) 2983, 2836, 2253, 1747, 1672, 1579, 1512, 1343, 1222, 1053, 1030, 735, 701. HRMS calcd for C\(_{28}\)H\(_{31}\)NO\(_7\): 493.2101, found: 493.2104. MS (70 eV): m/z (%): 493 (M\(^+\), 11.87), 451 (100).

11. Diethyl 1,4-diacyl-5-(4-nitrobenzyl)-3-phenyl-1\(H\)-pyrrole-2,2(3\(H\))-dicarboxylate.

According to the procedure of synthesis of 3i, the reaction of 2a (97.7 mg, 0.45 mmol), 1k (E, 87.3 mg, 0.3 mmol) in DMF under the catalysis of DBU (9.1 mg, 0.06 mmol) at 40 °C for 14 h affords 3k in the yield of 49% (75 mg). Yellow oil, \( ^1 \)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 8.19 \) (d, \( J = 8.8 \) Hz, 2 H), 7.48 (d, \( J = 8.8 \) Hz, 2 H), 7.35 (bs, 4 H), 7.15 (bs, 1 H), 5.00 (d, \( J = 15.6 \) Hz 1 H), 5.00 (s, 1 H), 4.81 (d, \( J = 15.6 \) Hz, 1 H), 4.46 ~ 4.35 (m, 1 H), 4.35 ~ 4.27 (m, 1 H), 3.66 ~ 3.55 (m, 1 H), 3.50 ~ 3.41 (m, 1 H), 1.98 (s, 3 H), 1.89 (s, 3 H), 1.32 (t, \( J = 7.2 \) Hz, 3 H), 0.90 (t, \( J = 7.2 \) Hz, 3 H). \( ^{13} \)C NMR (75.5 MHz, CDCl\(_3\)): 195.78, 170.42, 167.75, 164.45, 152.89, 146.57, 145.40, 136.22, 129.14, 128.74, 128.64, 123.57, 119.78, 79.26, 63.34, 62.52, 55.96, 32.92, 30.13, 25.21, 13.87, 13.31 ppm. IR (neat): \( \nu \)
(cm⁻¹) 2984, 2254, 1744, 1693, 1591, 1520, 1344, 1223, 1052, 1014, 860, 737, 701. HRMS calcd for C₂₇H₂₈N₂O₈: 508.1846, found: 508.1845. MS (70 eV): m/z (%): 508 (M⁺, 1.15), 43 (100).

12. Diethyl 1,4-diacetyl-5-benzyl-3-(4-methoxyphenyl)-1H-pyrrole-2,2(3H)-dicarboxylate.

According to the procedure of synthesis of 3i, the reaction of 2a (163.0 mg, 0.75 mmol), 1l (E, 136.0 mg, 0.5 mmol) in DMF under the catalysis of DBU (15.2 mg, 0.10 mmol) at 40 °C for 12 h affords 3l in the yield of 76% (187.4 mg). Yellow oil, ¹H NMR (300 MHz, CDCl₃): δ = 7.30 ~ 7.00 (m, 7 H), 6.80 (d, J = 8.1 Hz, 2 H), 4.823 (d, J = 15.9 Hz, 1 H), 4.824 (s, 1 H), 4.60 (d, J = 15.9 Hz, 1 H), 4.32 ~ 4.13 (m, 2 H), 3.72 (s, 3 H), 3.64 ~ 3.48 (m, 2 H), 2.04 (s, 3 H), 1.85 (s, 3 H), 1.21 (t, J = 7.2 Hz, 3 H), 0.88 (t, J = 7.2 Hz, 3 H). ¹³C NMR (75.5 MHz, CDCl₃): 195.59, 169.95, 167.54, 164.21, 159.42, 152.56, 136.73, 128.49, 128.35, 127.85, 126.29, 120.14, 113.61, 78.64, 62.54, 61.74, 55.00, 54.40, 32.16, 29.85, 24.83, 13.62, 13.21 ppm. IR (neat): ν (cm⁻¹) 2983, 2838, 1745, 1672, 1579, 1511, 1344, 1222, 1029, 840, 736, 700. HRMS calcd for C₂₈H₃₁NO₇: 493.2101, found: 493.2121. MS (70 eV): m/z (%): 493 (M⁺, 5.24), 332 (100).

13. Diethyl 1,4-diacetyl-5-benzyl-3-(4-chlorophenyl)-1H-pyrrole-2,2(3H)-dicarboxylate.
According to the procedure of synthesis of 3i, the reaction of 2a (97.7 mg, 0.45 mmol) and 1m (E, 84.0 mg, 0.3 mmol) in DMF under the catalysis of DBU (9.1 mg, 0.06 mmol) at 40 °C for 17 h affords 3m in the yield of 69% (103.0 mg). Yellow oil, 1H NMR (400 MHz, CDCl3): δ = 7.34 ~ 7.21 (m, 8 H), 7.14 (bs, 1 H), 4.90 (s, 1 H), 4.87 (d, J = 15.6 Hz 1 H), 4.64 (d, J = 15.6 Hz, 1 H), 4.39 ~ 4.30 (m, 1 H), 4.28 ~ 4.19 (m, 1 H), 3.70 ~ 3.61 (m, 1 H), 3.57 ~ 3.47 (m, 1 H), 2.11 (s, 3 H), 1.92 (s, 3 H), 1.27 (t, J = 7.2 Hz, 3 H), 0.93 (t, J = 7.2 Hz, 3 H). 13C NMR (100 MHz, CDCl3): 195.17, 169.98, 167.42, 164.13, 153.19, 136.48, 135.41, 134.26, 128.55, 127.87, 126.56, 119.78, 78.56, 62.87, 62.04, 54.19, 32.30, 30.04, 24.93, 13.72, 13.29 ppm. IR (neat): v (cm−1) 2983, 2253, 1747, 1673, 1583, 1492, 1345, 1222, 1054, 1014, 735, 700. HRMS calcd for C27H28ClNO6: 497.1605, found: 497.1602. MS (70 eV): m/z (%): 497 (M+, 2.46), 43 (100).

14. Diethyl 1-acetyl-4-benzoyl-5-benzyl-3-phenyl-1H-pyrrole-2,2(3H)-dicarboxylate.

According to the procedure of synthesis of 3i, the reaction of 2a (163.0 mg, 0.75 mmol) and 1n (E, 154.0 mg, 0.5 mmol) in DMF under the catalysis of DBU (15.2 mg, 0.10 mmol) at 40 °C for 20 h affords 3n in the yield of 66% (173.2 mg).
Yellow oil, $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.63 \sim 7.58$ (m, 2 H), 7.45 $\sim$ 7.35 (m, 1 H), 7.31 $\sim$ 7.24 (m, 4 H), 7.22 $\sim$ 7.16 (m, 8 H), 5.19 (s, 1 H), 4.40 $\sim$ 4.21 (m, 4 H), 3.53 (q, $J = 7.2$ Hz, 2 H), 2.03 (s, 3 H), 1.28 (t, $J = 7.2$ Hz, 3 H), 0.87 (t, $J = 7.2$ Hz, 3 H). $^{13}$C NMR (75.5 MHz, CDCl$_3$): 192.78, 170.08, 167.59, 164.70, 150.50, 139.13, 136.75, 136.17, 132.10, 129.21, 128.39, 128.24, 128.03, 127.93, 126.50, 122.53, 78.41, 62.58, 61.96, 55.92, 33.49, 24.65, 13.75, 13.21 ppm. IR (neat): $\nu$ (cm$^{-1}$) 2983, 1743, 1674, 1600, 1451, 1369, 1236, 1056, 1004, 735, 697. HRMS calcd for C$_{32}$H$_{31}$NO$_6$: 525.2151, found: 525.2145. MS (70 eV): m/z (%): 525 (M$^+$, 2.00), 105 (100).

15. Diethyl 1-acetyl-4-benzoyl-5-(4-methoxybenzyl)-3-phenyl-1H-pyrrole-2,2(3H)-dicarboxylate.

![Chemical Structure](image)

According to the procedure of synthesis of 3i, the reaction of 2a (97.7 mg, 0.45 mmol) and 1o (E, 101.4 mg, 0.3 mmol) in DMF under the catalysis of DBU (9.1 mg, 0.06 mmol) at 40 °C for 16 h affords 3o in the yield of 65% (108.3 mg). Yellow oil, $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.62$ (d, $J = 7.6$ Hz, 2 H), 7.43 (t, $J = 7.2$ Hz, 1 H), 7.31 (t, $J = 7.2$ Hz, 2 H), 7.22 $\sim$ 7.16 (m, 5 H), 7.13 (d, $J = 8.0$ Hz, 2 H), 6.83 (d, $J = 8.0$ Hz, 2 H), 5.10 (s, 1 H), 4.40 $\sim$ 4.26 (m, 2 H), 4.25 (d, $J = 16.4$ Hz, 1 H), 4.15 (d, $J = 16.4$ Hz, 1 H), 3.77 (s, 3 H), 3.54 (q, $J = 6.8$ Hz, 2 H), 2.08 (s, 3 H), 1.31 (t, $J = 6.8$ Hz, 3 H), 0.88 (t, $J = 6.8$ Hz, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): 192.88, 170.13, 167.69, 164.81, 158.22, 150.86, 139.21, 136.27, 132.16, 129.26, 129.00, 128.72, 128.30, 128.12, 128.01, 127.96, 122.41, 113.89, 78.45, 62.64, 62.02, 55.91, 55.13, 32.71, 24.71, 13.83, 13.29 ppm. IR (neat): $\nu$ (cm$^{-1}$) 2981, 2253, 1744, 1610, 1512, 1369, 1242, 1177, 1056, 1030, 725, 698.
HRMS calcd for C\textsubscript{33}H\textsubscript{33}NO\textsubscript{7}: 555.2257, found: 555.2266. MS (70 eV): m/z (%): 555 (M\textsuperscript{+}, 4.31), 43 (100).

16. Diethyl 1-acetyl-4-benzoyl-5-benzyl-3-(4-methoxyphenyl)-1\textsubscript{H}-pyrrole-2,2(3\textsubscript{H})-dicarboxylate.

![Chemical Structure](image)

According to the procedure of synthesis of 3\textit{i}, the reaction of 2\textit{a} (97.7 mg, 0.45 mmol) and 1\textit{p} (E, 101.4 mg, 0.3 mmol) in DMF under the catalysis of DBU (9.1 mg, 0.06 mmol) at 40 °C for 28 h affords 3\textit{p} in the yield of 67% (112.0 mg). Yellow oil, \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ = 7.63 (d, J = 7.2 Hz, 2 H), 7.43 (t, J = 7.2 Hz, 1 H), 7.34 ~ 7.25 (m, 4 H), 7.22 ~ 7.18 (m, 3 H), 7.14 (d, J = 8.0 Hz, 2 H), 6.74 (d, J = 8.0 Hz, 2 H), 5.14 (s, 1 H), 4.38 ~ 4.21 (m, 4 H), 3.70 (s, 3 H), 3.61 (q, J = 6.8 Hz, 2 H), 2.04 (s, 3 H), 1.29 (t, J = 7.2 Hz, 3 H), 0.94 (t, J = 7.2 Hz, 3 H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): 192.91, 170.13, 167.66, 164.78, 159.21, 150.16, 139.12, 136.83, 132.15, 130.37, 128.41, 128.27, 128.08, 128.04, 127.95, 126.51, 122.78, 113.35, 78.38, 62.57, 62.00, 55.43, 55.02, 33.50, 24.70, 13.79, 13.35 ppm. IR (neat): ν (cm\textsuperscript{-1}) 2982, 2837, 2253, 1744, 1608, 1511, 1447, 1243, 1177, 1056, 1030, 732, 698. HRMS calcd for C\textsubscript{33}H\textsubscript{33}NO\textsubscript{7}: 555.2257, found: 555.2261. MS (70 eV): m/z (%): 555 (M\textsuperscript{+}, 3.90), 105 (100).

17. Diethyl 1-acetyl-5-benzyl-4-(4-methoxybenzoyl)-3-phenyl-1\textsubscript{H}-pyrrole-2,2(3\textsubscript{H})-dicarboxylate.
According to the procedure of synthesis of 3i, the reaction of 2a (97.7 mg, 0.45 mmol) and 1q (E, 101.4 mg, 0.3 mmol) in DMF under the catalysis of DBU (9.1 mg, 0.06 mmol) at 40 °C for 46 h affords 3q in the yield of 61% (101.6 mg).

Yellow oil, $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.74$ (d, $J = 8.0$ Hz, 2 H), 7.34 ~ 7.14 (m, 10 H), 6.83 (d, $J = 8.4$ Hz, 2 H), 5.24 (s, 1 H), 4.40 ~ 4.17 (m, 4 H), 3.80 (s, 3 H), 3.54 (q, $J = 6.8$ Hz, 2 H), 2.03 (s, 3 H), 1.29 (t, $J = 6.8$ Hz, 3 H), 0.88 (t, $J = 6.8$ Hz, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): 191.19, 170.04, 167.72, 164.91, 163.18, 148.72, 136.90, 136.15, 131.50, 130.93, 129.31, 128.41, 128.03, 127.99, 126.53, 122.94, 113.63, 78.40, 62.61, 62.02, 56.25, 55.32, 33.79, 24.63, 13.81, 13.28 ppm. IR (neat): $\nu$ (cm$^{-1}$) 2981, 2253, 1744, 1676, 1598, 1455, 1304, 1247, 1169, 1055, 1026, 847, 734, 699. HRMS calcld for C$_{33}$H$_{33}$NO$_7$: 555.2257, found: 555.2260. MS (70 eV): m/z (%): 555 (M$^+$, 2.83), 135 (100).

18. Diethyl 1-acetyl-5-benzyl-4-(4-chlorobenzoyl)-3-phenyl-1H-pyrrole-2,2(3H)-dicarboxylate.

According to the procedure of synthesis of 3i, the reaction of 2a (163.0 mg, 0.75 mmol) and 1r (E, 171.5 mg, 0.5 mmol) in DMF under the catalysis of DBU (15.2 mg, 0.10 mmol) at 40 °C for 16 h affords 3r in the yield of 74% (206.8 mg).

Orange oil, $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.56$ (d, $J = 8.4$ Hz, 2 H), 7.32 ~
7.18 (m, 12 H), 5.16 (s, 1 H), 4.38 ~ 4.20 (m, 4 H), 3.54 (q, J = 7.2 Hz, 2 H), 2.04 (s, 3 H), 1.29 (t, J = 7.2 Hz, 3 H), 0.87 (t, J = 7.2 Hz, 3 H). $^{13}$C NMR (75.5 MHz, CDCl$_3$): 191.48, 170.10, 167.56, 164.63, 151.04, 138.37, 137.47, 136.60, 136.01, 129.45, 129.17, 128.56, 128.46, 128.02, 127.91, 126.60, 122.08, 78.46, 62.67, 62.04, 55.89, 33.55, 24.69, 13.76, 13.22 ppm. IR (neat): $\nu$ (cm$^{-1}$) 3267, 2995, 1755, 1720, 1641, 1611, 1384, 1362, 1258, 1219, 1061, 1014, 766, 702. HRMS calcd for C$_{32}$H$_{30}$NO$_6$Cl: 559.1762, found: 559.1757. MS (70 eV): m/z (%): 559 (M$^+$, 1.42), 139 (100).


The reaction of 2a (163.0 mg, 0.75 mmol) and 1s (E, 172 mg, 0.5 mmol) in DMF under the catalysis of DBU (15.2 mg, 0.10 mmol) at 40 °C for 22 h affords 3s in the yield of 51% (143.0 mg). White solid, m.p.: 90 ~ 91 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.35 ~ 7.01 (m, 13 H), 6.86 (t, J = 7.5 Hz, 1 H), 6.72 (d, J = 7.5 Hz, 1 H), 4.94 (s, 1 H), 4.85 (d, J = 15.6 Hz, 1 H), 4.52 (d, J = 15.6 Hz, 1 H), 4.21 ~ 4.03 (m, 2 H), 3.44 ~ 3.37 (m, 2 H), 1.84 (s, 3 H), 1.11 (t, J = 7.2 Hz, 3 H), 0.74 (t, J = 7.2 Hz, 3 H). $^{13}$C NMR (75.5 MHz, CDCl$_3$): 170.59, 166.70, 164.04, 153.44, 141.65, 135.76, 134.24, 132.72, 130.31, 128.81, 128.54, 128.15, 127.94, 127.83, 127.21, 126.73, 121.66, 79.19, 63.00, 62.39, 55.84, 31.81, 25.17, 13.67, 13.19 ppm. IR (neat): $\nu$ (cm$^{-1}$) 3503, 2926, 1760, 1740, 1695, 1613, 1305, 1265, 1229, 1150, 1106, 1080, 1018, 725, 699. HRMS calcd for C$_{31}$H$_{31}$NO$_7$S: 561.1821, found: 561.1818. MS (70 eV): m/z (%): 561 (M$^+$, 0.26), 233 (100).
20. Diethyl 1-acetyl-5-benzyl-4-cyano-3-phenyl-1H-pyrrole-2,2(3H)-dicarboxylate.

The reaction of 2a (163.0 mg, 0.75 mmol) and 1t (E, 114.5 mg, 0.5 mmol) in DMF under the catalysis of DBU (15.2 mg, 0.10 mmol) at 40 °C for 0.5 h affords 3t in the yield of 80% (178.0 mg). Orange solid, m.p.:119 ~ 120 °C. 1H NMR (300 MHz, CDCl3): δ = 7.39 ~ 7.26 (m, 10 H), 4.81 (s, 1 H), 4.48 (d, J = 15.9 Hz, 1 H), 4.35 (d, J = 15.9 Hz, 1 H), 4.38 ~ 4.28 (m, 2 H), 3.60 ~ 3.40 (m, 2 H), 2.03 (s, 3 H), 1.31 (t, J = 6.9 Hz, 3 H), 0.87 (t, J = 6.9 Hz, 3 H). 13C NMR (75.5 MHz, CDCl3): 168.95, 167.04, 163.75, 157.28, 135.04, 134.14, 129.26, 128.88, 128.43, 127.83, 127.24, 115.48, 94.51, 79.22, 63.11, 62.30, 54.28, 54.23, 34.47, 24.32, 13.87, 13.25 ppm. IR (neat): ν (cm⁻¹) 3461, 2928, 2210, 1757, 1741, 1678, 1625, 1379, 1362, 1236, 1058, 1008, 737, 697. HRMS calcd for C26H26N2O5: 446.1842, found: 446.1863. MS (70 eV): m/z (%): 404 (M⁺+H⁺-[CH3CO⁺]), 21.40), 43 (100).

21. Diethyl 1-acetyl-5-benzyl-4-formyl-3-phenyl-1H-pyrrole-2,2(3H)-dicarboxylate.

According to the procedure of synthesis of 3i, the reaction of 2a (163.0 mg, 0.75 mmol) and 1u (E, 116.0 mg, 0.5 mmol) in DMF under the catalysis of DBU (15.2
mg, 0.10 mmol) at 40 °C for 10 h affords 3u in the yield of 55% (123.0 mg). Yellow oil, 1H NMR (300 MHz, CDCl₃): δ = 9.89 (s, 1 H), 7.39 ~ 7.26 (m, 10 H), 4.92 (s, 1 H), 4.66 (d, J = 16.2 Hz, 1 H), 4.61 (d, J = 16.2 Hz, 1 H), 4.37 ~ 4.20 (m, 2 H), 3.60 ~ 3.39 (m, 2 H), 2.05 (s, 3 H), 1.30 (t, J = 7.2 Hz, 3 H), 0.88 (t, J = 7.2 Hz, 3 H). 13C NMR (75.5 MHz, CDCl₃): 185.05, 170.01, 167.29, 164.26, 157.87, 136.01, 135.71, 128.75, 127.94, 127.88, 127.03, 122.24, 79.22, 62.87, 62.10, 53.29, 31.44, 24.86, 13.74, 13.18 ppm. IR (neat): ν (cm⁻¹) 2919, 2850, 1743, 1684, 1652, 1613, 1454, 1261, 1208, 1055, 1015, 803, 739, 698. HRMS calcd for C₂₆H₂₇NO₆: 449.1838, found: 449.1845. MS (70 eV): m/z (%): 449 (M⁺, 5.06), 91 (100).

22. Trimethyl 1-acetyl-5-benzyl-3-phenyl-1H-pyrrole-2,2,4(3H)-tricarboxylate.

The reaction of 1a (E/Z = 1.1/1, 131.0 mg, 0.5 mmol) and 2b (141.8 mg, 0.75 mmol) in DMF under the catalysis of DBU (15.2 mg, 0.10 mmol) at 40 °C for 10 h affords 3v in the yield of 93% (210.0 mg). White solid, m.p.: 119-120 °C. 1H NMR (400 MHz, CDCl₃): δ = 7.35 ~ 7.20 (m, 10 H), 4.94 (d, J = 16.0 Hz, 1 H), 4.82 (s, 1 H), 4.67 (d, J = 16.0 Hz, 1 H), 3.83 (s, 3 H), 3.48 (s, 3 H), 3.05 (s, 3 H), 2.11 (s, 3 H). 13C NMR (100 MHz, CDCl₃): 169.54, 168.11, 164.78, 164.65, 153.38, 137.26, 136.41, 128.60, 127.93, 127.80, 127.76, 126.53, 112.70, 78.62, 54.17, 53.38, 52.09, 51.23, 32.18, 24.54 ppm. IR (neat): ν (cm⁻¹) 2950, 2889, 1741, 1703, 1672, 1631, 1438, 1391, 1242, 1207, 1067, 986, 740, 721, 671. HRMS calcd for C₂₅H₂₅NO₇: 451.1631, found: 451.1635. MS (70 eV): m/z (%): 451 (M⁺, 0.80), 43 (100).
23. 1-tert-Butyl 2,2-diethyl 4-methyl 5-benzyl-3-phenyl-1H-pyrrole-1,2,2,4(3H)-tetra-carboxylate.

\[
\begin{align*}
&\text{N} \\
&\text{CO}_2\text{CH}_3 \\
&\text{H}_3\text{CO} \\
&\text{CO}_2\text{CH}_3 \\
&\text{Boc} \\
&\text{H}_3\text{CO} \\
&\text{Ph}
\end{align*}
\]

3w

The reaction of 1a \((E/Z = 1.1/1, 131.0 \text{ mg, 0.5 mmol})\) and 2c \((156.0 \text{ mg, 0.75 mmol})\) in DMF under the catalysis of DBU \((15.2 \text{ mg, 0.10 mmol})\) at 40 °C for 3.5 h affords 3w in the yield of 80% \((215.0 \text{ mg})\). White solid, m.p.: 87~88 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.39 \text{ (d, } J = 7.2 \text{ Hz, 2 H}), 7.34 \sim 7.18 \text{ (m, 8 H), 4.93 \text{ (d, } J = 14.7 \text{ Hz, 1 H}), 4.79 \text{ (s, 1 H), 4.78 \text{ (d, } J = 14.7 \text{ Hz, 1 H), 4.38 \sim 4.23 \text{ (m, 2 H), 3.60 \sim 3.54 \text{ (m, 1 H) 3.48 \text{ (s, 3 H), 3.35 \sim 3.29 \text{ (m, 1 H), 1.28 \text{ (t, } J = 7.2 \text{ Hz, 3 H), 1.26 \text{ (s, 9 H), 0.87 \text{ (t, } J = 7.2 \text{ Hz, 3 H).}}\)}\) \(^{13}\)C NMR (75.5 MHz, CDCl\(_3\)): 168.18, 165.11, 164.71, 155.66, 150.40, 138.10, 137.88, 128.07, 128.29, 128.07, 127.85, 127.55, 125.99, 109.02, 83.11, 77.89, 62.37, 61.49, 54.66, 51.04, 31.98, 27.55, 13.98, 13.35 ppm. IR (neat): \(\nu \text{ (cm}^{-1}\) 2979, 1754, 1727, 1702, 1625, 1368, 1226, 1153, 1009, 731, 705. HRMS calcd for C\(_{30}\)H\(_{35}\)NO\(_8\): 537.2363, found: 537.2358. MS (70 eV): m/z (%): 537 (M\(^+\), 1.82), 57 (100).

24. 1-Benzyl 2,2-diethyl 4-methyl 5-benzyl-3-phenyl-1H-pyrrole-1,2,2,4(3H)-tetra-carboxylate.

\[
\begin{align*}
&\text{N} \\
&\text{CO}_2\text{CH}_3 \\
&\text{H}_3\text{CO} \\
&\text{CO}_2\text{CH}_3 \\
&\text{Cbz} \\
&\text{H}_3\text{CO} \\
&\text{Ph}
\end{align*}
\]

3x

The reaction of 1a \((E/Z = 1.1/1, 78.6 \text{ mg, 0.3 mmol})\) and 2d \((139.0 \text{ mg, 0.45 mmol})\) in DMF under the catalysis of DBU \((9.1 \text{ mg, 0.06 mmol})\) at 40 °C for 11 h
affords \(3x\) in the yield of 93% (159.0 mg). Colorless oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.34 \sim 7.18\) (m, 13 H), \(7.11 \sim 7.08\) (m, 2 H), \(5.00\) (s, 2 H), \(4.90\) (d, \(J = 14.4\) Hz, 1 H), \(4.85\) (s, 1 H), \(4.78\) (d, \(J = 14.4\) Hz, 1 H), \(4.27 \sim 4.15\) (m, 2 H), \(3.49\) (s, 3 H), \(3.34 \sim 3.25\) (m, 1 H), \(3.20 \sim 3.10\) (m, 1 H), \(1.17\) (t, \(J = 7.2\) Hz, 3 H), \(0.68\) (t, \(J = 7.2\) Hz, 3 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(168.00, 164.92, 164.30, 155.11, 151.66, 137.67, 137.42, 134.81, 128.27, 128.22, 127.89, 127.67, 126.08, 110.14, 77.85, 77.20, 67.99, 62.57, 61.59, 54.95, 51.19, 32.10, 13.77, 13.16\) ppm. IR (neat): \(v\) (cm\(^{-1}\)) 2986, 2901, 1737, 1702, 1631, 1393, 1226, 1056, 1018, 740, 697. HRMS calcd for C\(_{33}\)H\(_{33}\)NO\(_8\): 571.2206, found: 571.2205. MS (70 eV): m/z (%): 571 (M\(^+\), 1.28), 91 (100).

25. 2,2-Diethyl 4-methyl 5-benzyl-3-phenyl-1\(^H\)-pyrrole-2,2,4(3\(^H\))-tricarboxylate.

![Chemical structure](image)

The reaction of \(1a\) (\(E/Z = 1.1/1\), 52.4 mg, 0.2 mmol), \(2e\) (50.8 mg, 0.24 mmol) and DBU (42.6 mg, 0.28 mmol) in DMF at 40 \(^\circ\)C for 2 h affords \(3y\) in the yield of 87% (76.0 mg). White solid, m.p.: 97-98 \(^\circ\)C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.38 \sim 7.16\) (m, 10 H), \(5.05\) (s, 1 H), \(4.85\) (s, 1 H), \(4.43\) (d, \(J = 15.2\) Hz, 1 H), \(4.17\) \sim 4.04 (m, 2 H), \(4.00\) (d, \(J = 15.2\) Hz, 1 H), \(3.71 \sim 3.64\) (m, 1 H), \(3.56 \sim 3.48\) (m, 1 H), \(3.51\) (s, 3 H), \(1.09\) (t, \(J = 7.2\) Hz, 3 H), \(0.77\) (t, \(J = 7.2\) Hz, 3 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(168.57, 167.14, 165.82, 159.23, 138.95, 136.38, 128.80, 128.75, 128.53, 127.83, 127.16, 126.97, 102.93, 76.92, 62.36, 61.80, 53.42, 50.44, 33.39, 13.72, 13.27. IR (neat): \(v\) (cm\(^{-1}\)) 3371, 2994, 2885, 2814, 1726, 1678, 1598, 1432, 1267, 1211, 1130, 1094, 1052, 776, 739, 702 ppm. HRMS calcd for C\(_{25}\)H\(_{27}\)NO\(_6\): 437.1838, found: 437.1839. MS (70 eV): m/z (%): 437 (M\(^+\), 44.80), 91 (100).
Synthesis of 3y from 2-pyrrole 3w: 2-Pyrrole 3w (126.7 mg, 0.29 mmol) was dissolved in 4 mL of CH$_2$Cl$_2$ under 0 °C, CF$_3$CO$_2$H (1 mL, 14.5 mmol) was added and the mixture was stirred for 30 min, then was stirred for overnight. After the reaction was complete, 4 mL of H$_2$O was added and the aqueous phase was neutralized by 1 N NaOH. The reaction mixture was then extracted with CH$_2$Cl$_2$ (3 x 5 mL) and the combined organic phase was washed successively with saturated NaHCO$_3$, NaCl and dried over anhydrous MgSO$_4$. After removal of solvent under vacuum, the residue was purified by column chromatography on silica gel to give 84% (106 mg) of 3y.

The procedure for the synthesis of pyrrole 4

26. dimethyl 1-acetyl-5-benzyl-3-phenyl-2,3-dihydro-1H-pyrrole-2,4-dicarboxylate –e.

A mixture of 3v (270.6 mg, 0.6 mmol), lithium chloride (32.5 mg, 0.75 mmol), and water (15.5 mg, 0.85 mmol) in 2.0 mL of anhydrous dimethylformamide under nitrogen was stirred at 160-165 °C. The solution immediately became cloudy and began evolving CO$_2$. After stirring for 1h, the reaction mixture was cooling down and poured into 15 mL water with vigorous stirring. The gummy solid which formed was collected by filtration through glass wool, dissolved in dichloromethane, and dried with anhydrous MgSO$_4$. After the solution was concentrated under vacuum, the residual product was purified by column chromatography on silica gel to give white solid; yield: 54% (127.0 mg). m.p.: 134~135 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.36 ~ 7.20$ (m, 10 H), 4.92 (d, $J = 14.8$ Hz, 1 H), 4.30 (d, $J = 14.8$ Hz, 1 H), 4.59 (bs, 1 H), 4.29 (s, 1 H), 3.76 (s, 3
H) 3.58 (s, 3 H), 2.00 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): 170.63, 168.85, 165.24, 141.78, 137.15, 128.95, 128.51, 128.29, 127.59, 126.62, 126.32, 69.31, 52.87, 51.30, 49.90, 32.65, 24.29 ppm. IR (neat): $\nu$ (cm$^{-1}$) 2954, 2924, 2853, 1743, 1704, 1672, 1631, 1439, 1391, 1243, 1207, 1089, 986, 747, 721, 693. HRMS calcd for C$_{23}$H$_{23}$NO$_5$: 393.1576, found: 393.1578. MS (70 eV): m/z (%): 393 (M$^+$, 14.52), 91 (100).

**X-ray crystal structure of 3e.**
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3h

[Chemical structure image]
yxz-10-31 C

![Chemical structure](image)
Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012
yxz-10-27 C

3k
Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

yzx-10-26 C

3m
Electronic Supplementary Material (ESI) for Chemical Communications
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yxz-10-30 H
$\text{yxz-10-28 C}$

![Chemical structure diagram]
yxz-10-48 H
yxz-10-35 H
yxz-11-111 H

![Chemical structure diagram](image_url)
xyz-11-111 C
yxz-13-64 H

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yxz-13-64 C
yxz-13-23 H

Electronic Supplementary Material (ESI) for Chemical Communications
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Electronic Supplementary Material (ESI) for Chemical Communications

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yxz-11-105 H

4

[Chemical structure diagram]

[ spectral data ]
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$y_{xz-11-105\, H}$