Supporting Information

Palladium-Catalyzed Carbonylation of Yne-Esters Leading to γ -Alkylidene α,β -Unsaturated γ -Lactones

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General Information ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL JMN-270 spectrometer in CDCl_3 with tetramethylsilane as an internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and c = complex), coupling constant (Hz), integration, and interpretation. Infrared spectra (IR) were obtained on a Horiba FT-700 spectrometer. Mass spectra were obtained on a Shimadzu GCMS-QP 5000 instrument with ionization voltages of 70 eV. Elemental analyses were performed by the Elemental Analysis Section of Osaka University. High resolution mass spectra (HRMS) were obtained on a JEOL JMS-DX303. Analytical GC was carried out on a Shimadzu GC-14A gas chromatography, equipped with a flame ionization detector. Melting points were determined on a Yamato melting point apparatus and are uncorrected. Column chromatography was performed with SiO_2 (Merck SilicaGel 60 (230-400 mesh)).

Materials Toluene was distilled over CaH_2 . $[(\eta^3\text{-C}_3\text{H}_5)\text{PdCl}]_2$ was purchased from Strem Chemicals Inc. and was used as received. Dicyclohexylmethylamine was distilled prior to use. All starting materials were prepared as described below.

3,3-Dimethyl-oct-5-ynoyl chloride (1a) 3,3-Dimethyl-oct-5-ynoic acid was prepared from mesityl oxide and 3-keto-hexanoic acid methyl ester using a modification of the method of Johnson.¹⁾ The compound (**1a**) was prepared by the reaction of 3,3-dimethyl-oct-5-ynoic acid and oxalyl chloride and purification by bulb-to-bulb distillation. colorless oil. ^1H NMR (CDCl_3) δ : 1.10-1.15 (c, 9H), 2.15-2.19 (c, 4H), 2.98 (s, 2H). ^{13}C NMR (CDCl_3) δ : 12.4, 14.3, 26.4, 31.7, 34.6, 57.1, 75.7, 84.8, 171.6. IR (neat): 2974 m, 2937 m, 2879 m, 2850 w, 1807 s, 1707 w, 1469 m, 1435 w, 1390 m, 1371 m, 1335 w, 1323 w, 1201 w, 1167 w, 1139 w, 1030 w, 1001 m, 976 m, 910 w, 879 w, 783 m, 725 m, 563 w. MS, m/z (relative intensity, %): 188 ($\text{M}^+ + 2$, 12), 186 (M^+ , 45), 151 (10), 150 (16), 135 (18), 132 (16), 130 (48), 109 (18), 107 (27), 104 (15), 102 (43), 95 (24), 93 (18), 91 (32), 83 (14), 79 (24), 77 (33), 69 (11), 67 (100), 66 (40), 65 (43), 63 (14), 56 (14), 55 (29), 53 (40), 52 (15), 51 (46), 50 (13). Exact Mass Calcd for $\text{C}_{10}\text{H}_{15}\text{O}^{35}\text{Cl}$: 186.0811. Found: 186.0804.

3,3-Dimethyl-oct-5-ynoic acid pentafluorophenyl ester (1b) The compound (**1b**) was prepared by the reaction of pentafluorophenol and 3,3-dimethyl-oct-5-ynoyl chloride, which was prepared from 3,3-dimethyl-oct-5-ynoic acid and SOCl_2 and was purified by column chromatography on

Florisil. colorless oil. R_f 0.59 (hexane/EtOAc = 2/1). ^1H NMR (CDCl_3) δ : 1.14 (t, J = 7.6 Hz, 3H), 1.17 (s, 6H), 2.20 (tq, J = 2.3 Hz, 7.6 Hz, 2H), 2.25 (t, J = 2.3 Hz, 2H), 2.68 (s, 2H). ^{13}C NMR (CDCl_3) δ : 12.5, 14.4, 26.7, 32.4, 34.0, 43.9, 75.9, 84.5, 135-143(c, 6C), 167.7. IR (neat): 2976 m, 2939 m, 2881 w, 2667 w, 2461 w, 1790 s, 1655 w, 1522 s, 1469 m, 1435 w, 1392 w, 1371 w, 1354 w, 1321 w, 1255 w, 1201 w, 1180 m, 1142 m, 1086 s, 1024 s, 1005 s, 920 w, 887 w, 858 w, 783 w, 708 w, 619 w, 590 w, 561 w. MS, m/z (relative intensity, %): 334 (M^+ , 2), 225 (36), 155 (10), 151 (70), 109 (48), 95 (100), 93 (21), 91 (18), 83 (17), 81 (31), 79 (22), 77 (19), 69 (15), 67 (88), 65 (19), 56 (15), 55 (54), 53 (21), 51 (11). Anal. Calcd for C, 57.49; H, 4.52; F, 28.42. Found: C, 57.43; H, 4.76; F, 28.21.

1-Imidazol-1-yl-3,3-dimethyl-oct-5-yn-1-one (1c) The compound (**1c**) was prepared by the reaction of 3,3-dimethyl-oct-5-ynoic acid 1,1'-carbonyldiimidazole²⁾ and was purified by column chromatography on Florisil. colorless oil. R_f 0.24 (hexane/EtOAc = 1/1). ^1H NMR (CDCl_3) δ : 1.11 (t, J = 7.6 Hz, 3H), 1.16 (s, 6H), 2.16 (tq, J = 2.3 Hz, 7.6 Hz, 2H), 2.27 (t, J = 2.3 Hz, 2H), 2.88 (s, 2H), 7.10 (s, 1H), 7.52 (s, 1H), 8.21 (s, 1H). ^{13}C NMR (CDCl_3) δ : 12.4, 14.3, 27.1, 32.2, 34.2, 44.2, 76.1, 84.8, 116.0, 130.7, 129.2, 136.2, 167.8. IR (neat): 3122 w, 2972 s, 2937 m, 2877 m, 1734 s, 1527 w, 1473 s, 1392 m, 1377 s, 1321 m, 1273 s, 1232 s, 1200 m, 1167 w, 1109 w, 1078 m, 1041 w, 972 m, 897 w, 839 w, 796 w, 754 m, 650 m, 623 w. MS, m/z (relative intensity, %): 218 (M^+ , 5), 151 (17), 110 (31), 109 (37), 95 (100), 92 (21), 91 (16), 82 (35), 80 (23), 79 (14), 77 (16), 69 (66), 68 (27), 66 (87), 64 (15), 54 (40), 53 (15). Exact Mass Calcd for $\text{C}_{13}\text{H}_{18}\text{N}_2\text{O}$: 218.1419. Found: 218.1416.

3,3-Dimethyl-oct-5-ynoic acid 2,5-dioxo-pyrrolidin-1-yl ester (1d) The compound (**1d**) was prepared from N-hydroxysuccineimide and 3,3-dimethyl-oct-5-ynoyl chloride by a procedure similar to that used for **1b** and was purified by column chromatography on Florisil. colorless oil. R_f 0.24 (hexane/EtOAc = 1/1). ^1H NMR (CDCl_3) δ : 1.11 (t, J = 7.6 Hz, 3H), 1.14 (s, 6H), 2.16 (tq, J = 1.9 Hz, 7.6 Hz, 2H), 2.21 (t, J = 1.9 Hz, 2H), 2.60 (s, 2H), 2.82 (s, 4H). ^{13}C NMR (CDCl_3) δ : 12.4, 14.3, 25.5, 26.5, 32.4, 34.1, 41.5, 75.9, 84.5, 166.9, 169.2. IR (neat): 2973 s, 2937 m, 2879 w, 1813 s, 1786 s, 1743 s, 1469 m, 1431 m, 1369 s, 1321 m, 1205 s, 1151 w, 1065 s, 993 w, 920 w, 841 w, 814 w, 758 m, 700 w, 648 m, 579 w. MS, m/z (relative intensity, %): 265 (M^+ , 0), 151 (28), 116 (11), 109 (33), 108 (39), 107 (12), 95 (85), 93 (23), 91 (12), 83 (75), 81 (12), 79 (16), 77 (13), 67 (100), 65 (13), 56 (29), 55 (92), 53 (14). Exact Mass Calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_4$: 265.1314. Found: 265.1318.

3,3-Dimethyl-oct-5-ynethioic acid S-phenyl ester (1e) The compound (**1e**) was prepared from thiophenol and 3,3-dimethyl-oct-5-ynoyl chloride by a procedure similar to that used for **1b** and was purified by bulb-to-bulb distillation. colorless oil. colorless oil. R_f 0.66 (hexane/EtOAc = 2/1). ^1H NMR (CDCl_3) δ : 1.12 (s, 6H), 1.15 (t, J = 7.3 Hz, 3H), 2.20 (tq, J = 2.3 Hz, 7.3 Hz, 2H), 2.21 (t, J = 2.3 Hz, 2H), 2.69 (s, 2H), 7.40 (s, 5H). ^{13}C NMR (CDCl_3) δ : 12.4, 14.3, 26.9, 32.3, 34.7, 53.2, 76.4, 84.3, 128.2, 129.1, 129.2, 134.3, 195.8. IR (neat): 3076 w, 2970 s, 2935 m, 2912 m, 2875 m, 1803 w, 1707 s, 1583 w, 1477 m, 1469 m, 1441 m, 1389 w, 1367 w, 1321 m, 1194 w, 1167 w, 1138 w, 1068 w, 1036 m, 1007 s, 1001 s, 908 w, 877 w, 783 w, 744 s, 688 s, 536 w. MS, m/z (relative intensity, %):

260 (M^+ , 1), 151 (45), 110 (13), 109 (71), 95 (94), 91 (11), 81 (26), 79 (16), 77 (18), 69 (13), 67 (100), 65 (35), 55 (39), 53 (16), 51 (16). Exact Mass Calcd for $C_{16}H_{20}OS$: 260.1235. Found: 260.1233.

3,3-Dimethyl-oct-5-ynoic acid pyridin-2-yl ester (1f) The compound (**1f**) was prepared from 2-hydroxypyridine (2-pyridone) and 3,3-dimethyl-oct-5-ynoyl chloride by a procedure similar to that used for **1b** and was purified by column chromatography on Florisil. colorless oil. R_f 0.17 (hexane/EtOAc = 5/1).

1H NMR ($CDCl_3$) δ : 1.14 (t, J = 7.4 Hz, 3H), 1.20 (s, 6H), 2.19 (tq, J = 2.5 Hz, 7.4 Hz, 2H), 2.28 (t, J = 2.5 Hz, 2H), 2.63 (s, 2H), 7.07 (ddd, J = 0.8 Hz, 1.0 Hz, 7.9 Hz, 1H), 7.22 (ddd, J = 1.0 Hz, 4.9 Hz, 7.3 Hz, 1H), 7.78 (ddd, J = 2.0 Hz, 7.3 Hz, 7.9 Hz, 1H), 8.41 (ddd, J = 0.8 Hz, 2.0 Hz, 4.9 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ : 12.4, 14.3, 26.8, 32.4, 33.8, 44.7, 76.4, 84.2, 116.5, 121.9, 139.3, 148.6, 157.9, 170.2. IR (neat): 3060 w, 2970 s, 2935 m, 2877 m, 1761 s, 1678 w, 1591 s, 1576 m, 1468 s, 1433 s, 1390 w, 1352 m, 1323 m, 1201 s, 1147 s, 1103 s, 995 w, 937 m, 910 w, 795 w, 773 w, 746 m. MS, m/z (relative intensity, %): 245 (M^+ , 0.1), 161 (18), 109 (13), 96 (100), 95 (58), 93 (11), 91 (10), 83 (42), 79 (10), 78 (15), 67 (44), 55 (25), 53 (10), 51 (10). Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N, 5.71. Found: C, 73.20; H, 7.76; N, 5.55.

3,3-Dimethyl-oct-5-ynoic acid 6-methyl-pyridin-2-yl ester (1g) The compound (**1g**) was prepared from 6-methyl-2-hydroxypyridine and 3,3-dimethyl-oct-5-ynoyl chloride by a procedure similar to that used for **1b** and was purified by column chromatography on Florisil. colorless oil. R_f 0.29 (hexane/EtOAc = 5/1).

1H NMR ($CDCl_3$) δ : 1.14 (t, J = 7.6 Hz, 3H), 1.18 (s, 6H), 2.19 (tq, J = 2.3 Hz, 7.6 Hz, 2H), 2.27 (t, J = 2.3 Hz, 2H), 2.53 (s, 3H), 2.62 (s, 2H), 6.88 (d, J = 7.9 Hz, 1H), 7.06 (d, J = 7.2 Hz, 1H), 7.66 (dd, J = 7.2 Hz, 7.9 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ : 12.5, 14.4, 26.8, 32.4, 33.8, 44.7, 76.4, 84.2, 113.1, 121.2, 139.3, 156.9, 157.9, 170.1. IR (neat): 2973 m, 2949 w, 1814 w, 1757 s, 1602 s, 1577 w, 1454 s, 1369 w, 1354 w, 1323 w, 1265 w, 1201 s, 1184 m, 1142 m, 1105 s, 1022 w, 993 w, 951 m, 814 w, 762 w, 723 w, 544 w. MS, m/z (relative intensity, %): 259 (M^+ , 0.4), 175 (11), 151 (11), 110 (100), 109 (82), 95 (59), 92 (11), 83 (35), 81 (18), 80 (11), 67 (32), 65 (16), 55 (21), 52 (13). Exact Mass Calcd for $C_{16}H_{21}NO_2$: 259.1572. Found: 259.1579.

3,3-Dimethyl-oct-5-ynoic acid pyridin-4-yl ester (1h) The compound (**1h**) was prepared from 6-methyl-2-hydroxypyridine and 3,3-dimethyl-oct-5-ynoyl chloride by a procedure similar to that used for **1b** and was purified by column chromatography on Florisil. colorless oil. R_f 0.14 (hexane/EtOAc = 2/1).

1H NMR ($CDCl_3$) δ : 1.09 (t, J = 7.3 Hz, 3H), 1.15 (s, 6H), 2.18 (tq, J = 2.3 Hz, 7.3 Hz, 2H), 2.24 (t, J = 2.3 Hz, 2H), 2.58 (s, 2H), 7.09 (d, J = 5.9 Hz, 2H), 8.60 (d, J = 5.9 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ : 12.4, 14.3, 26.8, 32.3, 33.9, 44.7, 76.2, 84.4, 116.9, 151.3, 157.3, 169.2. IR (neat): 3033 w, 2972 s, 2935 m, 2877 m, 1765 s, 1583 s, 1495 m, 1469 m, 1412 m, 1354 m, 1323 m, 1228 s, 1198 s, 1147 m, 1108 s, 993 w, 935 m, 910 w, 847 m, 522 m. MS, m/z (relative intensity, %): 245 (M^+ , 3), 151 (36), 136 (10), 109 (34), 96 (34), 95 (100), 93 (16), 91 (11), 83 (14), 81 (18), 79 (13), 78 (14), 77 (11), 67 (66), 65 (11), 56 (11), 55 (38), 53 (13), 51 (22). Exact Mass Calcd for $C_{15}H_{19}NO_2$: 245.1416. Found: 245.1410.

3,3-Dimethyl-hept-5-ynoic acid pyridin-2-yl ester 3,3-Dimethyl-hept-5-ynoic acid was prepared from mesityl oxide and 3-keto-*n*-valeric acid methyl ester using a modification of the method of Johnson.¹⁾ The compound was prepared from 2-hydroxypyridine and 3,3-dimethyl-hept-5-ynoyl chloride by a procedure similar to that used for **1b** and was purified by column chromatography on Florisil. colorless oil. *R_f* 0.14 (hexane/EtOAc = 5/1). ¹H NMR (CDCl₃) δ: 1.19 (s, 6H), 1.82 (t, *J* = 2.5 Hz, 3H), 2.27 (q, *J* = 2.5 Hz, 2H), 2.63 (s, 2H), 7.07 (ddd, *J* = 0.8 Hz, 1.0 Hz, 7.9 Hz, 1H), 7.22 (ddd, *J* = 1.0 Hz, 4.9 Hz, 7.3 Hz, 1H), 7.78 (ddd, *J* = 2.0 Hz, 7.3 Hz, 7.9 Hz, 1H), 8.41 (ddd, *J* = 0.8 Hz, 2.0 Hz, 4.9 Hz, 1H). ¹³C NMR (CDCl₃) δ: 3.4, 26.8, 32.4, 33.8, 44.7, 76.1, 77.9, 116.5, 121.9, 139.3, 148.6, 157.8, 170.2. IR (neat): 3060 w, 2962 s, 2922 m, 1761 s, 1678 w, 1593 s, 1574 m, 1469 s, 1433 s, 1390 m, 1354 m, 1329 m, 1201 s, 1146 s, 1103 s, 995 m, 937 m, 912 w, 843 w, 772 w, 746 m, 622 w, 555 w, 509 w. MS, *m/z* (relative intensity, %): 231 (*M*⁺, 0.7), 147 (31), 137 (28), 96 (100), 95 (25), 94 (11), 93 (10), 83 (47), 81 (66), 79 (19), 78 (20), 77 (15), 67 (37), 55 (36), 53 (50), 51 (23). Anal. Calcd for C₁₅H₁₉NO₂: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.46; H, 7.29; N, 6.04.

3,3-Dimethyl-6-phenyl-hex-5-ynoic acid pyridin-2-yl ester Isophoroneoxide was prepared by an epoxidation of isophorone³⁾. 4,4-dimethyl-hept-6-yn-2-one was prepared by the modified Eschenmoser fragmentation, as reported by Tanabe⁴⁾. 4,4-dimethyl-7-phenyl-hept-6-yn-2-one was prepared from iodobenzene and 4,4-dimethyl-7-phenyl-hept-6-yn-2-one by a Sonogashira reaction. 3,3-dimethyl-6-phenyl-hex-5-ynoic acid was prepared from 4,4-dimethyl-7-phenyl-hept-6-yn-2-one by the bromoform reaction¹⁾. The compound was prepared from 2-hydroxypyridine and 3,3-dimethyl-6-phenyl-hex-5-ynoyl chloride by a procedure similar to that used for **1b** and was purified by column chromatography on Florisil. colorless oil. *R_f* 0.14 (hexane/EtOAc = 5/1). ¹H NMR (CDCl₃) δ: 1.29 (s, 6H), 2.57 (s, 2H), 2.71 (s, 2H), 7.05 (ddd, *J* = 0.8 Hz, 1.0 Hz, 7.9 Hz, 1H), 7.21 (ddd, *J* = 1.0 Hz, 4.9 Hz, 7.3 Hz, 1H), 7.27-7.30 (m, 3H), 7.42 (m, 2H), 7.78 (ddd, *J* = 2.0 Hz, 7.3 Hz, 7.9 Hz, 1H), 8.41 (ddd, *J* = 0.8 Hz, 2.0 Hz, 4.9 Hz, 1H). ¹³C NMR (CDCl₃) δ: 27.0, 32.8, 34.1, 44.9, 83.0, 87.3, 116.5, 122.0, 123.8, 127.7, 128.2, 131.6, 139.4, 148.6, 157.9, 170.1. IR (neat): 3059 w, 2964 m, 2904 w, 2877 m, 1761 s, 1593 m, 1574 w, 1491 w, 1469 m, 1433 m, 1354 w, 1329 w, 1261 s, 1200 s, 1144 m, 1103 s, 1024 m, 937 w, 912 w, 796 s, 758 m, 692 m, 526 w. MS, *m/z* (relative intensity, %): 293 (*M*⁺, 2), 209 (55), 156 (45), 143 (24), 142 (17), 141 (17), 129 (17), 128 (13), 116 (11), 115 (96), 96 (100), 95 (20), 91 (18), 89 (15), 83 (76), 78 (20), 77 (10), 67 (24), 65 (11), 63 (14), 55 (38), 51 (17). Exact Mass Calcd for C₁₉H₁₉NO₂: 293.1416. Found: 293.1419.

3,3-Dimethyl-6-thiophen-2-yl-hex-5-ynoic acid pyridin-2-yl ester The compound was prepared by a procedure similar to that used for **3,3-dimethyl-6-phenyl-hex-5-ynoic acid pyridin-2-yl ester** and was purified by column chromatography on Florisil. colorless oil. *R_f* 0.33 (hexane/EtOAc = 2/1). ¹H NMR (CDCl₃) δ: 1.27 (s, 6H), 2.59 (s, 2H), 2.69 (s, 2H), 6.94 (dd, *J* = 3.6 Hz, 5.3 Hz, 1H), 7.07 (ddd, *J* = 0.8 Hz, 1.0 Hz, 7.9 Hz, 1H), 7.13-7.26 (c, 3H), 7.78 (ddd, *J* = 2.0 Hz, 7.3 Hz, 7.9 Hz, 1H), 8.41 (ddd, *J* = 0.8 Hz, 2.0 Hz, 4.9 Hz, 1H). ¹³C NMR (CDCl₃) δ: 27.0, 33.0, 34.2, 44.9,

76.1, 91.4, 116.5, 122.0, 123.8, 126.1, 126.8, 131.2, 139.4, 148.6, 157.8, 170.0. IR (neat): 3105 w, 2964 m, 2933 w, 2875 w, 1759 s, 1676 w, 1655 w, 1593 s, 1574 w, 1469 s, 1431 s, 1390 w, 1356 m, 1328 w, 1201 s, 1145 m, 1105 s, 1045 w, 995 w, 937 w, 847 m, 771 w, 744 w, 701 m, 509 w. MS, m/z (relative intensity, %): 299 (M^+ , 7), 215 (27), 205 (28), 163 (15), 162 (69), 161 (15), 148 (15), 147 (14), 143 (12), 128 (12), 121 (73), 97 (19), 96 (100), 95 (15), 93 (10), 83 (70), 78 (27), 77 (38), 69 (14), 67 (18), 63 (14), 55 (32), 51 (24). Exact Mass Calcd for $C_{17}H_{17}NO_2S$: 299.0980. Found: 299.0982.

6-(4-Methoxy-phenyl)-3,3-dimethyl-hex-5-ynoic acid pyridin-2-yl ester The compound was prepared by a procedure similar to that used for **3,3-dimethyl-6-phenyl-hex-5-ynoic acid pyridin-2-yl ester** and was purified by column chromatography on Florisil. colorless oil. R_f 0.29 (hexane/EtOAc = 2/1). 1H NMR ($CDCl_3$) δ : 1.27 (s, 6H), 2.54 (s, 2H), 2.70 (s, 2H), 3.79 (s, 3H), 6.81 (d, J = 8.9 Hz, 2H), 7.06 (ddd, J = 0.8 Hz, 1.0 Hz, 7.9 Hz, 1H), 7.21 (ddd, J = 1.0 Hz, 4.9 Hz, 7.3 Hz, 1H), 7.35 (d, J = 8.9 Hz, 2H), 7.76 (ddd, J = 2.0 Hz, 7.3 Hz, 7.9 Hz, 1H), 8.41 (ddd, J = 0.8 Hz, 2.0 Hz, 4.9 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ : 26.9, 32.8, 34.1, 44.8, 55.2, 82.7, 85.6, 113.8, 115.8, 116.4, 121.9, 132.9, 139.3, 148.6, 157.8, 159.1, 170.1. IR (neat): 3064 w, 2962 m, 2933 w, 2837 w, 1761 s, 1606 s, 1592 s, 1573 m, 1510 s, 1469 s, 1433 s, 1354 w, 1329 w, 1290 s, 1248 s, 1200 s, 1174 s, 1105 s, 1034 m, 995 w, 937 w, 833 s, 746 w, 536 w. MS, m/z (relative intensity, %): 323 (M^+ , 2), 229 (26), 187 (17), 186 (100), 172 (16), 171 (10), 145 (66), 128 (11), 115 (12), 102 (23), 96 (49), 95 (11), 83 (62), 78 (15), 77 (10), 67 (15), 55 (29), 51 (11). Exact Mass Calcd for $C_{20}H_{21}NO_3$: 323.1521. Found: 323.1512.

3,3-Dimethyl-6-(4-nitro-phenyl)-hex-5-ynoic acid pyridin-2-yl ester The compound was prepared by a procedure similar to that used for **3,3-dimethyl-6-phenyl-hex-5-ynoic acid pyridin-2-yl ester** and was purified by recrystallization. White solid. mp 68 °C. R_f 0.26 (hexane/EtOAc = 2/1). 1H NMR ($CDCl_3$) δ : 1.29 (s, 6H), 2.64 (s, 2H), 2.70 (s, 2H), 7.07 (ddd, J = 0.8 Hz, 1.0 Hz, 7.9 Hz, 1H), 7.22 (ddd, J = 1.0 Hz, 4.9 Hz, 7.3 Hz, 1H), 7.55 (d, J = 8.9 Hz, 2H), 7.78 (ddd, J = 2.0 Hz, 7.3 Hz, 7.9 Hz, 1H), 8.16 (d, J = 8.9 Hz, 2H), 8.41 (ddd, J = 0.8 Hz, 2.0 Hz, 4.9 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ : 27.1, 32.7, 34.1, 44.8, 81.6, 93.6, 116.4, 122.1, 123.5, 130.7, 132.3, 139.4, 146.7, 148.6, 157.7, 169.8. IR (KBr): 3112 w, 2960 w, 2933 w, 2220 w, 1757 s, 1593 s, 1514 s, 1468 m, 1434 m, 1348 s, 1327 m, 1308 w, 1242 w, 1203 s, 1161 s, 1099 s, 991 w, 933 w, 910 w, 854 m, 769 w, 750 m, 690 w, 513 w. MS, m/z (relative intensity, %): 338 (M^+ , 0), 282 (10), 254 (20), 160 (11), 141 (11), 102 (11), 96 (100), 95 (27), 83 (35), 78 (12), 67 (19), 55 (15). Anal. Calcd for $C_{19}H_{18}N_2O_4$: C, 67.44; H, 5.36; N, 8.28. Found: C, 67.28; H, 5.22; N, 8.26.

2-Ethoxycarbonyl-2-pent-2-ynyl-succinic acid 1-ethyl ester 4-pyridin-2-yl ester Bromoacetic acid *t*-amyl ester was prepared from bromoacetyl bromide and *t*-amyl alcohol. 2-ethoxycarbonyl-2-pent-2-ynyl-succinic acid 1-ethyl ester was prepared from diethylmalonate, bromoacetic acid *t*-amyl ester and 1-bromo-2-pentyne using a modification of the method of Kraus⁵. The compound was prepared from 2-hydroxypyridine and 2-ethoxycarbonyl-2-pent-2-ynyl-

succinic acid 1-ethyl ester by a procedure similar to that used for **1b** and was purified by column chromatography on Florisil. colorless oil. *R_f* 0.29 (hexane/EtOAc = 2/1). ¹H NMR (CDCl₃) δ: 1.19 (t, *J* = 7.6 Hz, 3H), 1.24 (t, *J* = 7.3 Hz, 6H), 2.11 (tq, *J* = 2.3 Hz, 7.6 Hz, 2H), 3.00 (t, *J* = 2.3 Hz, 2H), 3.44 (s, 2H), 4.21 (q, *J* = 7.3 Hz, 4H), 7.07 (ddd, *J* = 0.8 Hz, 1.0 Hz, 7.9 Hz, 1H), 7.22 (ddd, *J* = 1.0 Hz, 4.9 Hz, 7.3 Hz, 1H), 7.78 (ddd, *J* = 2.0 Hz, 7.3 Hz, 7.9 Hz, 1H), 8.41 (ddd, *J* = 0.8 Hz, 2.0 Hz, 4.9 Hz, 1H). ¹³C NMR (CDCl₃) δ: 12.3, 13.9, 14.0, 23.9, 36.9, 55.2, 62.0, 73.3, 85.6, 116.3, 122.1, 139.4, 148.5, 157.4, 168.8, 168.8. IR (neat): 3062 w, 2978 s, 2939 m, 1739 s, 1657 w, 1618 w, 1592 s, 1574 w, 1541 w, 1470 s, 1433 s, 1408 w, 1367 s, 1327 m, 1294 s, 1196 s, 1144 s, 1095 m, 1072 m, 1047 s, 1016 m, 941 m, 862 m, 773 w, 744 w. MS, *m/z* (relative intensity, %): 361 (*M*⁺, 0), 316 (2), 267 (32), 194 (12), 193 (100), 165 (23), 161 (14), 160 (10), 147 (11), 136 (28), 121 (14), 119 (12), 109 (13), 99 (13), 96 (84), 95 (26), 93 (17), 91 (39), 79 (12), 78 (35), 77 (34), 69 (16), 67 (38), 65 (23), 57 (13), 55 (18), 53 (17), 51 (23). Exact Mass Calcd for C₁₉H₂₃NO₆: 361.1525. Found: 361.1528.

6-Cyclohexyl-3,3-bis-ethoxycarbonyl-hex-5-ynoic acid pyridin-2-yl ester The compound was prepared by a procedure similar to that used for **2-ethoxycarbonyl-2-pent-2-ynyl-succinic acid 1-ethyl ester 4-pyridin-2-yl ester** and was purified by column chromatography on Florisil. colorless oil. *R_f* 0.26 (hexane/EtOAc = 2/1). ¹H NMR (CDCl₃) δ: 1.25 (t, 6H), 1.22-1.45 (c, 6H), 1.65-1.75 (c, 4H), 2.32 (m, 1H), 3.02 (d, *J* = 2.3 Hz, 2H), 3.45 (s, 2H), 4.22 (q, 4H), 7.07 (ddd, *J* = 0.8 Hz, 1.0 Hz, 7.9 Hz, 1H), 7.23 (ddd, *J* = 1.0 Hz, 4.9 Hz, 7.3 Hz, 1H), 7.76 (ddd, *J* = 2.0 Hz, 7.3 Hz, 7.9 Hz, 1H), 8.38 (ddd, *J* = 0.8 Hz, 2.0 Hz, 4.9 Hz, 1H). ¹³C NMR (CDCl₃) δ: 13.9, 24.0, 24.7, 25.8, 28.9, 32.7, 37.0, 55.4, 62.0, 74.0, 88.6, 116.4, 122.1, 139.4, 148.5, 157.5, 168.9, 168.9. IR (neat): 3060 w, 2981 m, 2931 s, 2854 m, 1766 s, 1739 s, 1657 w, 1593 m, 1574 w, 1468 s, 1433 s, 1365 m, 1294 s, 1194 s, 1144 s, 1097 m, 1070 m, 1049 m, 1014 w, 941 w, 887 w, 862 w, 760 w, 557 w, 509 w. MS, *m/z* (relative intensity, %): 415 (*M*⁺, 0), 247 (21), 229 (13), 214 (15), 201 (19), 173 (22), 145 (13), 121 (14), 105 (14), 96 (100), 95 (30), 93 (21), 91 (37), 81 (27), 79 (35), 78 (29), 77 (26), 67 (52), 65 (16), 55 (38), 53 (18), 51 (12). Exact Mass Calcd for C₂₃H₂₉NO₆: 415.1995. Found: 415.1992.

6-Phenyl-hex-5-ynoic acid pyridin-2-yl ester 6-Phenyl-hex-5-ynoic acid was prepared from iodobenzene and 5-ynoic acid by a Sonogashira reaction. The compound was prepared from 2-hydroxypyridine and 2-ethoxycarbonyl-2-pent-2-ynyl-succinic acid 1-ethyl ester by a procedure similar to that used for **1b** and was purified by column chromatography on Florisil. colorless oil. *R_f* 0.31 (hexane/EtOAc = 2/1). ¹H NMR (CDCl₃) δ: 2.04 (tt, *J* = 6.8 Hz, 7.3 Hz, 2H), 2.58 (t, *J* = 6.8 Hz, 2H), 2.83 (t, *J* = 7.3 Hz, 2H), 7.05 (ddd, *J* = 0.8 Hz, 1.0 Hz, 7.9 Hz, 1H), 7.19-7.29 (c, 4H), 7.39 (m, 2H), 7.78 (ddd, *J* = 2.0 Hz, 7.3 Hz, 7.9 Hz, 1H), 8.41 (ddd, *J* = 0.8 Hz, 2.0 Hz, 4.9 Hz, 1H). ¹³C NMR (CDCl₃) δ: 18.9, 23.7, 33.2, 81.6, 88.5, 116.3, 121.9, 123.5, 127.6, 128.1, 131.5, 139.3, 148.4, 157.7, 171.1. IR (neat): 3059 w, 2941 w, 2906 w, 2227 w, 1765 s, 1591 m, 1574 m, 1491 m, 1469 m, 1433 s, 1377 w, 1196 s, 1128 s, 1047 w, 995 w, 910 w, 841 w, 759 m, 692 m, 623 w, 509 w. MS, *m/z* (relative intensity, %): 265 (*M*⁺, 1), 209 (28), 143 (19), 141 (13), 129 (12), 128 (78), 127 (11), 115 (51), 96 (100), 95 (12), 89 (11), 67 (11), 65 (10), 63 (11), 55 (59), 51 (11). Anal. Calcd for C₁₇H₁₅NO₂: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.96; H, 5.84; N, 5.19.

3,3-Bis-ethoxycarbonyl-non-6-ynoic acid pyridin-2-yl ester

The compound was prepared by a procedure similar to that used for 2-ethoxycarbonyl-2-pent-2-ynyl-succinic acid 1-ethyl ester 4-pyridin-2-yl ester and was purified by column chromatography on Florisil. colorless oil.

R_f 0.26 (hexane/EtOAc = 2/1). ^1H NMR (CDCl_3) δ : 1.07 (t, J = 7.5 Hz, 3H),

1.24 (t, J = 7.1 Hz, 6H), 2.11 (tq, J = 2.1 Hz, 7.5 Hz, 2H), 2.23 (tq, J = 2.1 Hz, 7.3 Hz, 2H), 2.33 (t, J = 7.3 Hz, 2H), 3.30 (s, 2H), 4.20 (q, J = 7.1 Hz, 4H), 7.06 (ddd, J = 0.8 Hz, 1.0 Hz, 7.9 Hz, 1H), 7.21 (ddd, J = 1.0 Hz, 4.9 Hz, 7.3 Hz, 1H), 7.76 (ddd, J = 2.0 Hz, 7.3 Hz, 7.9 Hz, 1H), 8.36 (ddd, J = 0.8 Hz, 2.0 Hz, 4.9 Hz, 1H). ^{13}C NMR (CDCl_3) δ : 12.3, 13.9, 14.0, 14.5, 32.4, 37.5, 55.2, 61.8, 77.6, 82.7, 116.3, 122.1, 139.4, 148.5, 157.4, 168.6, 169.7. IR (neat): 3060 w, 2979 m, 2939 w, 2877 w, 1766 s, 1736 s, 1593 m, 1574 w, 1469 m, 1433 s, 1367 m, 1298 m, 1273 m, 1190 s, 1140 s, 1095 m, 1066 m, 1022 m, 995 w, 966 w, 931 w, 860 w, 775 w, 744 w, 509 w. MS, m/z (relative intensity, %): 375 (M^+ , 0), 235 (28), 206 (11), 161 (13), 154 (15), 135 (23), 133 (24), 105 (17), 96 (100), 91 (11), 85 (11), 79 (19), 78 (24), 69 (24). Exact Mass (CI^+) Calcd for $\text{C}_{20}\text{H}_{26}\text{NO}_6$: 376.1760. Found: 376.1768.

Typical Procedure for Cyclocarbonylation A 50-mL stainless autoclave was charged with $[(\eta^3\text{-C}_3\text{H}_5)\text{PdCl}]_2$ (9.1 mg, 0.025 mmol), triphenylphosphine (19.7 mg, 0.075 mmol), 3,3-dimethyl-oct-5-ynoic acid pyridin-2-yl ester (**1f**) (122.6 mg, 0.5 mmol), dicyclohexylmethylamine (0.11 mL, 0.5 mmol) and toluene (2.5 mL). The system was flushed with 10 atm of carbon monoxide three times, and then filled with carbon monoxide (1 atm). The autoclave was then immersed in an oil bath at 120 °C. After 20 hours had elapsed, it was removed from the oil bath, allowed to cool for ca. 1 h and the gases were then released. The contents were transferred to a round-bottom flaske with toluene, and the volatiles were removed in vacuo. The residue was subjected to column chromatography on silica-gel (eluent; hexane/EtOAc = 10/1) to give 3-ethyl-5,5-dimethyl-4,5-dihydro-2H-cyclopenta[b]furan-2-one (**2**) (75 mg, 84 % yield) as a white solid.

3-Ethyl-5,5-dimethyl-4,5-dihydro-2H-cyclopenta[b]furan-2-one (**2**)

white solid. mp 84 °C. R_f 0.37 (hexane/EtOAc = 5/1). ^1H NMR (CDCl_3) δ : 1.17 (t, J = 7.6 Hz, 3H), 1.28 (s, 6H), 2.34 (tq, J = 1.7 Hz, 7.6 Hz, 2H), 2.61 (t, J = 1.7 Hz, 2H), 5.45 (s, 1H). ^{13}C NMR (CDCl_3) δ : 11.8, 17.9, 29.2, 39.3, 48.3, 119.5, 120.7, 151.1, 160.4, 174.3. IR (KBr): 2966 m, 2943 w, 2870 w, 1799 m, 1766 s, 1649 s, 1473 m, 1458 w, 1417 m, 1348 m, 1251 m, 1147 m, 1063 m, 1022 w, 947 m, 901 s, 835 s, 739 w, 658 w. MS, m/z (relative intensity, %): 178 (M^+ , 23), 164 (11), 163 (100), 135 (42), 107 (29), 105 (14), 91 (54), 83 (31), 79 (29), 77 (18), 69 (13), 67 (15), 65 (22), 55 (64), 53 (29), 52 (13), 51 (26), 50 (10). Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{O}_2$: C, 74.13; H, 7.92. Found: C, 73.95; H, 7.81.

3,5,5-Trimethyl-4,5-dihydro-2H-cyclopenta[b]furan-2-one (**3**)

white solid. mp 117 °C. R_f 0.27 (hexane/EtOAc = 5/1). ^1H NMR (CDCl_3) δ : 1.26 (s, 6H), 1.88 (t, J = 1.3 Hz, 3H), 2.53 (q, J = 1.3 Hz, 2H), 5.44 (s, 1H). ^{13}C NMR (CDCl_3) δ : 9.0, 29.1, 38.7, 48.1, 115.0, 119.7, 151.1, 161.6, 175.1. IR (KBr): 3076 w, 2962 w, 2927 w, 2870 w, 1955 w, 1770 s, 1693 w, 1658 s, 1469 w, 1415 m, 1379 m, 1362 w, 1309 m, 1273 m, 1147 m, 1109 w, 1053 m, 982 m, 906 w, 864 s, 748 m, 717 m, 644 w, 577 w. MS, m/z

(relative intensity, %): 164 (M^+ , 24), 149 (100), 121 (59), 93 (26), 91 (19), 83 (22), 77 (23), 55 (26), 53 (31), 52 (10), 51 (18). Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 73.01; H, 7.09.

5,5-Dimethyl-3-phenyl-4,5-dihydro-2H-cyclopenta[b]furan-2-one (4)

colorless oil. R_f 0.31 (hexane/EtOAc = 5/1). 1H NMR ($CDCl_3$) δ : 1.35 (s, 6H), 2.91 (s, 2H), 5.67 (s, 1H), 7.32 (t, J = 7.3 Hz, 1H), 7.44 (dd, J = 6.9 Hz, 7.3 Hz, 2H), 7.85 (d, J = 6.9 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ : 29.0, 41.4, 48.8, 117.0, 122.3, 127.0, 128.2, 128.6, 130.4, 151.0, 160.6, 172.2. IR (neat): 3084 w, 3057 w, 2960 m, 2931 w, 2866 w, 1795 s, 1766 s, 1645 s, 1495 m, 1448 m, 1421 m, 1329 m, 1284 w, 1215 w, 1142 m, 1036 w, 916 s, 899 s, 835 w, 723 s, 748 w, 692 s, 671 w, 538 m. MS, m/z (relative intensity, %): 226 (M^+ , 50), 211 (57), 183 (71), 155 (24), 154 (20), 153 (17), 141 (16), 129 (13), 128 (17), 127 (15), 116 (14), 115 (40), 114 (13), 113 (10), 105 (14), 91 (15), 89 (23), 88 (13), 83 (82), 82 (13), 77 (28), 76 (22), 75 (15), 65 (18), 64 (12), 55 (100), 53 (20), 51 (38), 50 (14). Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.33; H, 6.23.

5,5-Dimethyl-3-thiophen-2-yl-4,5-dihydro-2H-cyclopenta[b]furan-2-one (5)

white solid. mp 69-70 °C. R_f 0.43 (hexane/EtOAc = 2/1). 1H NMR ($CDCl_3$) δ : 1.34 (s, 6H), 2.79 (s, 2H), 5.66 (s, 1H), 7.10 (dd, J = 3.5 Hz, 4.9 Hz, 2H), 7.37 (d, J = 4.9 Hz, 2H), 7.62 (d, J = 3.5 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ : 28.9, 40.6, 49.0, 113.0, 122.6, 126.3, 127.7, 132.6, 151.0, 157.2, 171.3. IR (KBr): 3083 w, 2958 w, 2931 w, 2904 w, 2866 w, 2360 w, 2341 w, 1772 s, 1643 m, 1622 m, 1520 w, 1469 w, 1365 w, 1275 w, 1227 w, 1147 w, 1130 m, 1103 w, 1024 w, 953 w, 923 m, 879 m, 840 m, 820 m, 762 w, 721 m, 687 s, 577 w, 513 w. MS, m/z (relative intensity, %): 232 (M^+ , 83), 217 (67), 190 (13), 189 (95), 161 (21), 128 (19), 121 (20), 115 (11), 83 (100), 80 (18), 77 (25), 68 (17), 63 (18), 55 (67), 53 (18), 51 (18), 50 (10). Anal. Calcd for $C_{13}H_{12}O_2S$: C, 67.21; H, 5.21; S, 13.80. Found: C, 67.01; H, 5.08; S, 13.77.

3-(4-Methoxy-phenyl)-5,5-dimethyl-4,5-dihydro-2H-cyclopenta[b]furan-2-one (6)

pale yellow solid. mp 110 °C. R_f 0.17 (hexane/EtOAc = 5/1). 1H NMR ($CDCl_3$) δ : 1.34 (s, 6H), 2.85 (s, 2H), 3.82 (s, 3H), 5.60 (s, 1H), 6.93 (d, J = 8.8 Hz, 2H), 7.79 (d, J = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ : 29.0, 41.3, 48.7, 55.2, 114.0, 116.7, 121.2, 123.0, 128.4, 151.0, 158.3, 159.4, 172.4. IR (KBr): 3083 w, 3008 w, 2962 w, 2933 w, 2898 w, 2870 w, 2837 w, 1797 m, 1757 s, 1703 w, 1641 m, 1606 m, 1574 w, 1510 s, 1466 w, 1423 w, 1335 m, 1296 w, 1252 s, 1184 m, 1140 m, 1119 w, 1030 m, 916 m, 899 s, 847 m, 810 m, 667 w, 590 w, 546 m. MS, m/z (relative intensity, %): 256 (M^+ , 45), 241 (45), 214 (11), 213 (73), 185 (14), 145 (12), 115 (12), 102 (18), 83 (100), 76 (17), 63 (12), 55 (68), 53 (14), 51 (11), 50 (10). Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.75; H, 6.28.

5,5-Dimethyl-3-(4-nitro-phenyl)-4,5-dihydro-2H-cyclopenta[b]furan-2-one (7)

white solid. mp 197 °C. R_f 0.37 (hexane/EtOAc = 2/1). 1H NMR ($CDCl_3$) δ : 1.39 (s, 6H), 2.97 (s, 2H), 5.85 (s, 1H), 8.03 (d, J = 8.6 Hz, 2H), 8.26 (d, J = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ : 28.8, 41.7, 49.4, 115.3, 123.9, 125.5, 127.5, 136.8, 146.8, 150.9,

164.2, 171.4. IR (KBr): 2964 w, 1808 w, 1772 m, 1763 s, 1640 m, 1616 m, 1597 m, 1513 s, 1469 w, 1420 w, 1348 m, 1332 m, 1318 m, 1285 w, 1145 w, 1107 w, 917 w, 905 w, 858 m, 843 w, 770 w, 687 w, 531 w. MS, m/z (relative intensity, %): 271 (M^+ , 42), 257 (23), 256 (100), 228 (66), 200 (17), 198 (24), 182 (23), 154 (20), 153 (35), 152 (44), 150 (15), 139 (13), 128 (13), 116 (15), 114 (17), 113 (18), 102 (19), 96 (14), 91 (17), 90 (12), 89 (16), 88 (17), 87 (12), 86 (14), 85 (11), 84 (11), 83 (99), 82 (14), 77 (20), 76 (30), 64 (21), 63 (32), 62 (12), 61 (11), 55 (95), 54 (11), 53 (13), 51 (17), 50 (15). Anal. Calcd for $C_{15}H_{13}NO_4$: C, 66.41; H, 4.83; N, 5.16. Found: C, 66.26; H, 4.64; N, 5.22.

3-Ethyl-2-oxo-2,4-dihydro-cyclopenta[*b*]furan-5,5-dicarboxylic acid diethyl ester (8) colorless oil. R_f 0.35 (hexane/EtOAc = 2/1). 1H NMR ($CDCl_3$) δ : 1.21 (t, J = 7.6 Hz, 3H), 1.29 (t, J = 6.8 Hz, 6H), 2.39 (q, J = 7.6 Hz, 2H), 3.41 (s, 2H), 4.25 (q, J = 6.8 Hz, 4H), 5.72 (s, 1H). ^{13}C NMR ($CDCl_3$) δ : 11.5, 14.0, 18.0, 31.6, 62.5, 66.8, 106.4, 123.1, 155.5, 157.0, 169.2, 173.1. IR (neat): 3109 w, 2979 m, 2939 m, 2908 w, 1799 s, 1734 s, 1657 s, 1463 m, 1425 m, 1389 m, 1367 m, 1261 s, 1180 s, 1124 m, 1097 m, 1055 s, 1007 m, 943 w, 891 s, 858 w, 831 w, 793 w, 621 w, 573 w. MS, m/z (relative intensity, %): 294 (M^+ , 10), 222 (19), 221 (100), 193 (25), 165 (13), 147 (13), 137 (10), 121 (11), 120 (10), 119 (19), 93 (12), 91 (41), 77 (19), 65 (18), 55 (18), 53 (21), 51 (19). Anal. Calcd for $C_{15}H_{14}O_2$: C, 61.22; H, 6.16. Found: C, 60.94; H, 6.12.

3-Cyclohexyl-2-oxo-2,4-dihydro-cyclopenta[*b*]furan-5,5-dicarboxylic acid diethyl ester (9) white solid. mp 82 °C. R_f 0.44 (hexane/EtOAc = 2/1). 1H NMR ($CDCl_3$) δ : 1.27 (t, J = 7.3 Hz, 6H), 1.25-1.99 (c, 6H), 2.44 (m, 1H), 3.43 (s, 2H), 4.25 (q, J = 7.3 Hz, 4H), 5.71 (s, 1H). ^{13}C NMR ($CDCl_3$) δ : 14.0, 25.8, 26.0, 31.1, 32.2, 34.8, 62.5, 66.8, 106.3, 126.6, 155.6, 156.0, 169.3, 172.7. IR (KBr): 3107 w, 2987 w, 2931 m, 2854 m, 1795 s, 1729 s, 1657 m, 1450 m, 1419 w, 1389 w, 1371 m, 1300 m, 1257 s, 1182 s, 1120 m, 1095 m, 1051 m, 978 m, 926 w, 908 m, 874 m, 831 m, 804 w, 739 w, 652 w, 604 w. MS, m/z (relative intensity, %): 348 (M^+ , 4), 276 (23), 275 (100), 247 (11), 201 (10), 173 (12), 167 (14), 145 (17), 131 (11), 117 (11), 115 (10), 107 (14), 105 (12), 93 (31), 91 (31), 81 (19), 79 (24), 77 (29), 67 (35), 65 (13), 55 (38), 53 (14). Anal. Calcd for $C_{19}H_{24}O_6$: C, 65.50; H, 6.94. Found: C, 65.21; H, 6.85.

3-Phenyl-4,5-dihydro-2H-cyclopenta[*b*]furan-2-one (10) white solid. mp 103 °C. R_f 0.39 (hexane/EtOAc = 2/1). 1H NMR ($CDCl_3$) δ : 2.99 (dt, J = 3.0 Hz, 3.6 Hz, 2H), 3.10 (t, J = 3.6 Hz, 2H), 5.86 (t, J = 3.0 Hz, 1H), 7.30 (tt, J = 1.3 Hz, 7.4 Hz, 1H), 7.44 (dd, J = 7.2 Hz, 7.4 Hz, 2H), 7.90 (dd, J = 1.3 Hz, 7.2 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ : 25.4, 33.5, 112.4, 116.3, 127.0, 128.1, 128.7, 130.4, 153.9, 161.6, 172.7. IR (KBr): 3107 w, 3068 w, 2906 w, 2843 w, 2360 w, 2341 w, 1792 w, 1745 s, 1643 m, 1619 m, 1493 w, 1448 m, 1412 m, 1327 w, 1255 w, 1184 w, 1139 m, 1036 w, 984 w, 916 s, 785 s, 740 m, 692 m, 671 w, 640 w, 540 m. MS, m/z (relative intensity, %): 198 (M^+ , 36), 142 (17), 141 (19), 128 (21), 115 (33), 63 (15), 55 (100). Anal. Calcd for $C_{13}H_{10}O_2$: C, 78.77; H, 5.09. Found: C, 78.50; H, 5.08.

3-Ethyl-2-oxo-4,5-dihydro-2H-benzofuran-6,6-dicarboxylic acid diethyl ester (11) colorless oil. *R_f* 0.37 (hexane/EtOAc = 2/1). ¹H NMR (CDCl₃) δ: 1.10 (t, *J* = 7.6 Hz, 3H), 1.24 (t, *J* = 7.0 Hz, 6H), 2.27-2.33 (c, 4H), 2.81 (t, *J* = 6.2 Hz, 2H), 4.18-4.23 (c, 4H), 5.91 (s, 1H). ¹³C NMR (CDCl₃) δ: 12.2, 13.9, 17.1, 19.6, 28.7, 54.4, 62.1, 104.6, 127.3, 145.3, 150.2, 169.4, 169.9. IR (neat): 2979 s, 2939 m, 2908 w, 1778 s, 1732 s, 1672 m, 1651 m, 1464 m, 1446 m, 1390 w, 1367 m, 1281 s, 1244 s, 1159 s, 1092 s, 1072 s, 1026 s, 945 s, 901 m, 845 m, 771 w, 694 w, 661 w, 630 w. MS, *m/z* (relative intensity, %): 308 (*M*⁺, 7), 236 (28), 235 (100), 207 (67), 189 (14), 161 (19), 133 (12), 119 (15), 117 (13), 107 (12), 105 (20), 91 (29), 79 (20), 77 (13), 67 (16), 65 (15). Exact Mass Calcd for C₁₆H₂₀O₆: 308.1260. Found: 308.1262.

2-Ethyl-pent-2-enoic acid pyridin-2-yl ester (12) colorless oil. *R_f* 0.40 (hexane/EtOAc = 2/1). ¹H NMR (CDCl₃) δ: 1.09 (t, *J* = 7.4 Hz, 3H), 1.10 (t, *J* = 7.4 Hz, 3H), 2.19 (dq, *J* = 7.4 Hz, 7.4 Hz, 2H), 2.28 (q, *J* = 7.4 Hz, 2H), 7.06 (m, 1H, 3-H), 7.07 (ddd, *J* = 0.8 Hz, 1.0 Hz, 7.9 Hz, 1H), 7.22 (ddd, *J* = 1.0 Hz, 4.9 Hz, 7.3 Hz, 1H), 7.78 (ddd, *J* = 2.0 Hz, 7.3 Hz, 7.9 Hz, 1H), 8.41 (ddd, *J* = 0.8 Hz, 2.0 Hz, 4.9 Hz, 1H). ¹³C NMR (CDCl₃) δ: 13.2, 13.9, 20.0, 22.0, 116.7, 121.7, 132.4, 139.3, 146.9, 148.5, 158.5, 165.9. IR (neat): 3059 w, 2970 s, 2935 m, 2875 m, 1732 s, 1657 m, 1616 m, 1591 s, 1574 m, 1543 w, 1469 s, 1433 s, 1381 w, 1302 m, 1286 m, 1207 s, 1149 s, 1128 s, 1109 s, 1088 s, 1014 m, 995 w, 945 m, 916 w, 858 w, 764 m, 514 w. MS, *m/z* (relative intensity, %): 205 (*M*⁺, 0.1), 176 (16), 111 (35), 67 (13), 55 (100). Exact Mass Calcd for C₁₂H₁₅NO₂: 205.1103. Found: 205.1107.

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12