Supplementary Information

Rh(I)-Catalyzed CO Gas-Free Cyclohydrocarbonylation of Alkynes with Formaldehyde to *α,β*-Butenolides

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General Information. ^{1}H NMR and ^{13}C NMR were recorded on a JEOL JNM-ECP500 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, and m = multiplet), coupling constant (Hz), integration, and interpretation. Infrared spectra (IR) were obtained on a JASCO FT/IR-420 spectrometer; absorption peaks are reported in reciprocal centimeters with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were obtained on a SHIMADZU GCMS-QP 5000 instrument with ionization voltages of 70 eV. High resolution mass spectra (HRMS) were obtained on a JEOL JMS-700. Analytical GC was carried out on a HITACHI G-3900 gas chromatography, equipped with a flame ionization detector. Melting point was obtained on Yanaco MP-500D. Column chromatography was performed on SiO_2 (preparation of acetylenes: MERCK Silica gel 60; cyclocarbonylation: KANTO Silica gel 60).

Materials. $[RhCl(cod)]_2$ was prepared using the method reported.[1] 1,3-Bis(diphenylphosphino)propane (dppp), triphenylphosphine-3,3’,3”-trisulfonic acid trisodium salt (TPPTS), and sodium dodecylsulfate (SDS) were purchased from Aldrich, Fluka, and Wako, respectively. Formalin was used as a 37% aqueous solution (including 8% of methanol) purchased from Nacalai Tesque. Diphenylacetylene (Eq. 2), *o*-Phthalaldehyde (Eq 3), 4-Octyne (Table 2, entry 1), Ethynyl benzene (Table 2, entry 2) and 1-Phenyl-1-propyne (Table 2, entry 4) were purchased from TCI, Wako, Aldrich, TCI and Pfaltz & Bauer. Other alkynes were prepared as described bellow.

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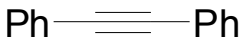
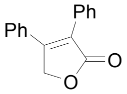
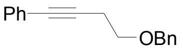
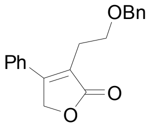
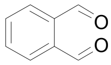
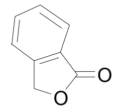
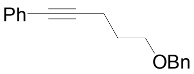
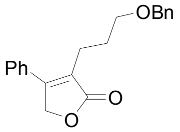
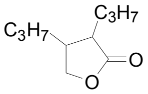
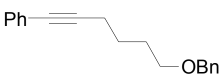
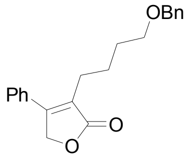
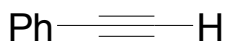
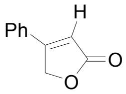
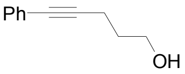
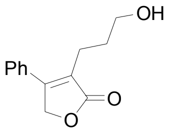
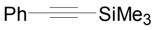
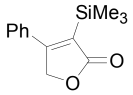
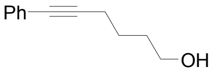
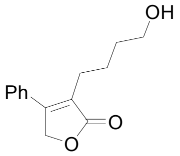
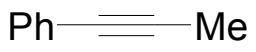
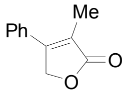
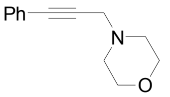
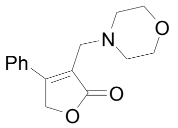
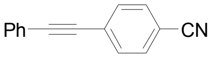
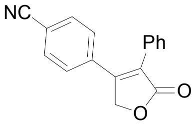
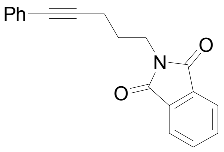
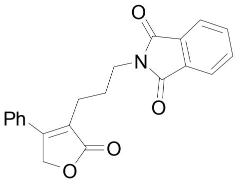
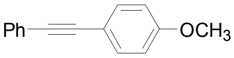
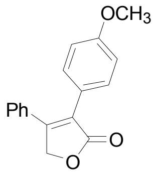
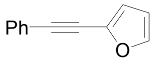
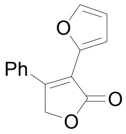
	**1**		**2**		**19**		**20**
	**3**		**4**		**21**		**22**
	**5**		**6**		**23**		**24**
	**7**		**8**		**25**		**26**
	**9**		**10**		**27**		**28**
	**11**		**12**		**29**		**30**
	**13**		**14**		**31**		**32**
	**15**		**16**				
	**17**		**17**				

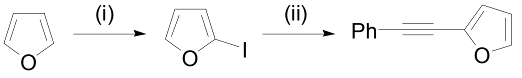
Alkyne 9 (Table 2, entry 3). To a solution of ethylmagnesium bromide (4.00 g, 30 mmol) in THF (5 ml) was added dropwise a solution of ethynylbenzene (2.04 g, 20 mmol) in THF (10 ml) over a period of 30 min at 10 °C and then the mixture was stirred at room temperature until the evolution of ethane gas subsided. The mixture was cooled to 10 °C, and a solution of trimethylsilyl chloride (3.26 g, 30 mmol) in THF (5 ml) was added dropwise over a period of 10 min. The mixture was poured into 2 *N* HCl aq. (15 ml), and an organic layer was separated. The aqueous layer was extracted with ether (2 x 10 ml), and the combined organic layers were washed with water (2 x 15 ml) and brine (15 ml), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica-gel (eluent; hexane, R_f 0.35) to give alkyne **9** (3.24 g, 18.6 mmol) in 93% yield. Colorless oil; R_f

0.35 (hexane); ^{1}H NMR (CDCl$_3$) δ 0.26 (s, 9H), 7.29-7.49 (m, 5H); ^{13}C NMR (CDCl$_3$) δ 0.0, 94.1, 105.1, 123.1, 128.2, 128.5, 131.9; IR (KBr) 2960 w, 2899 w, 2160 s, 1597 w, 1488 m, 1444 w, 1410 w, 1250 s, 1219 w, 1027 w, 866 m, 756 m, 690 w, 644 w, 537 w; MS, m/z (relative intensity, %) 175 (32), 174 (78), 161 (42), 160 (69), 159 (100); exact mass calcd for 174.0865, found 174.0862.

Alkyne 13 (Table 2, entry 5). A mixture of ethynylbenzene (1.02 g, 10 mmol), 4-bromobenzonitrile (2.18 g, 12 mmol), PdCl$_2$(PPh$_3$)$_2$ (140.4 mg, 0.2 mmol), PPh$_3$ (104.9 mg, 0.4 mmol), CuI (76.2 mg, 0.4 mmol) and Et$_2$NH (20 ml) was stirred at room temperature for 30 h. The reaction mixture was concentrated in vacuo, and the residue was purified by column chromatography on silica-gel (eluent; hexane/AcOEt = 20/1, R_f 0.17) to give alkyne **13** (2.03 g, 10 mmol) in 100% yield. White solid; mp 90-95 °C (hexane/AcOEt = 10/1); ^{1}H NMR (CDCl$_3$) δ 7.36-7.41 (m, 3H), 7.51-7.57 (m, 2H), 7.62 (dd, J = 8.6 Hz, J = 17 Hz, 5H); ^{13}C NMR (CDCl$_3$) δ 87.7, 93.8, 111.4, 118.5, 122.2, 128.2, 128.5, 129.1, 131.8, 132.0, 132.1, 132.6, 133.4; IR (KBr) 3856 w, 3651 w, 3087 w, 2372 w, 2226 w, 2214 m, 1928 w, 1686 w, 1656 w, 1604 m, 1502 m, 1442 w, 1408 w, 1272 w, 1175 w, 1070 w, 922 w, 844 s, 763 s, 692 s, 558 m, 532 m, 461 w; MS, m/z (relative intensity, %) 204 (20), 203 (100), 202 (11), 102 (23), 88 (13), 75 (11); exact mass calcd for 203.0735, found 203.0735.

Alkyne 15 (Table 2, entry 6). Alkyne **15** was obtained by the same procedure, using 4-bromoanisole in place of 4-bromobenzonitrile, as that of alkyne **13**. Pale yellow solid; mp 51-55 °C (hexane); R_f 0.24 (hexane/AcOEt = 10/1); ^{1}H NMR (CDCl$_3$) δ 3.83 (s, 3H), 6.89 (d, J = 8.6 Hz, 2H), 7.30-7.39 (m, 3H), 7.48 (d, J = 8.6 Hz, 2H), 7.52 (d, J = 6.1 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ 55.3, 88.0, 89.3, 114.0, 115.4, 123.6, 127.9, 128.3, 133.0, 159.6; IR (KBr) 3856 w, 3651 w, 2994 w, 2835 w, 2217 w, 1655 w, 1604 m, 1594 m, 1509 s, 1440 w, 1288 m, 1246 s, 1180 m, 1108 w, 1029 m, 834 m, 812 w, 755 m, 692 m, 524 m, 472 w; MS, m/z (relative intensity, %) 209 (17), 208 (100), 193 (51), 165 (37), 104 (14); exact mass calcd for 208.0888, found 208.0896.

Alkyne 17 (Table 2, entry 7).

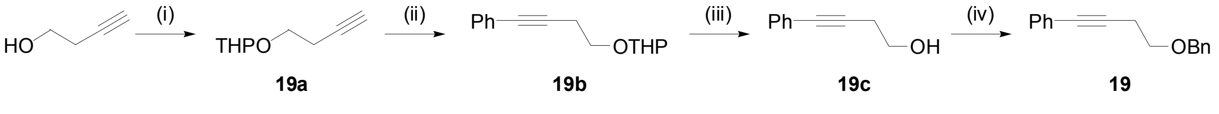


17a **17**

(i) To a cold (-78 °C) solution of furan (1.0 g, 15 mmol) in ether (10 ml) was added dropwise ^{n}BuLi (1.6 M in hexane 12.5 ml, 20 mmol) over a period of 15 min, and the mixture was stirred for 30 min at -78 °C, for 1 h at 0 °C and for 1.5 h at room temperature. After the mixture was cooled to -78 °C, I_2 (5.1 g, 20 mmol) in ether (20 ml) was added dropwise over a period of 30 min, and then the mixture was allowed to warm to room temperature and stirred for 24 h. The mixture was added saturated Na_2SO_3 aq. (20 ml), and an organic layer was separated. The aqueous layer was extracted with ether (3 x 15 ml), and the combined organic layers were washed with brine (2 x 20 ml), dried over $MgSO_4$, and evaporated. The residue was purified by column chromatography on silica-gel (eluent; hexane, R_f 0.47) to give **17a** (2.39 g, 12.3 mmol) in 82% yield.

(ii) A mixture of $PdCl_2(PPh_3)_2$ (211 mg, 0.3 mmol), PPh_3 (157 mg, 0.6 mmol), **17a** (2.39 g, 12 mmol), ethynyl benzene (1.53 g, 15 mmol) and CuI (114 mg, 0.6 mmol) in triethylamine (30 ml) was stirred at room temperature for 72 h. The reaction mixture was filtered and concentrated in vacuo. To the residue was added ether (20 ml) and water (10 ml), the whole was shaken vigorously, and an organic layer was separated. The aqueous layer was extracted with ether (2 x 15 ml), and the combined organic layers were washed with water (2 x 10 ml) and the brine (15 ml), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica-gel (eluent; hexane), and distilled by bulb-to-bulb distillation (1.2 mmHg, 120 °C) to give alkyne **17** (1.13 g, 6.69 mmol) in 54% yield. Colorless oil; R_f 0.33 (hexane/AcOEt = 100/1); ^{1}H NMR ($CDCl_3$) δ 6.42 (dd, J = 1.8 Hz, J = 3.1 Hz, 1H), 6.65 (d, J = 3.1 Hz, 1H), 7.34 (t, J = 3.7 Hz, 4H), 7.42 (s, 1H), 7.52 (dd, J = 3.1 Hz, J = 6.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 79.4, 93.2, 111.0, 115.2, 122.3, 128.4, 128.7, 131.4, 132.5, 137.1, 143.6; IR (neat) 3060 w, 2208 w, 1881 w, 1725 w, 1594 m, 1572 m, 1494 s, 1478 s, 1443 s, 1291 w, 1215 m, 1165 m, 1138 w, 1074 w, 1013 s, 929 m, 885 w, 813 w, 755 m, 688 m, 592 w; MS, m/z (relative intensity, %) 169 (40), 168 (100), 140 (63), 139 (99), 138 (11), 114 (36), 113 (21), 89 (12), 87 (15), 86 (10), 70 (11), 63 (15); exact mass calcd for 168.0575, found 168.0577.

Acetylene 19 (Table 2, entry 8).



(i) To a cold (0 °C) solution of 3-butyn-1-ol (1.45 g, 20 mmol), *p*-toluenesulfonic acid (114.1 mg, 0.6 mmol) in Et_2O (30 ml) was added dropwise 3,4-dihydro-2*H*-pyran (3.37 g, 40 mmol) over a period of 15 min, and the mixture was stirred at room temperature for 8 h. The reaction mixture was poured into saturated $NaHCO_3$ aq. (10 ml), and an organic layer was separated. The aqueous layer was extracted with ether (3 x 10 ml), and the combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica-gel (eluent; hexane/AcOEt=20/1) to give **19a** (2.63 g, 17.1 mmol) in 85% yield.

(ii) A mixture of $PdCl_2(PPh_3)_2$ (210.6 mg, 0.3 mmol), PPh_3 (157.4 mg, 0.6 mmol), CuI (114.3 mg, 0.6 mmol), **19a** (2.63 g, 17.1 mmol) and Et_2NH(30 ml) was stirred at room temperature for 12 h. After concentration of the reaction mixture, the residue was purified by column chromatography on silica-gel (eluent; hexane/AcOEt = 20/1) to give **19b** (3.78 g, 16.4 mmol) in 96% yield.

(iii) A mixture of *p*-toluenesulfonic acid (25.9 mg, 0.14 mmol), **19b** (1.57 g, 6.8 mmol) and CH_3OH (15 ml) was stirred at 60 °C for 4 d. The reaction mixture was poured into saturated $NaHCO_3$ aq. (10 ml), and concentrated in vacuo. The mixture was poured into Et_2O (20 ml) and the organic layer was separated. The aqueous layer was extracted with ether (3 x 10 ml), and the combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica-gel (eluent; hexane/AcOEt = 4/1, R_f 0.12) to give **19c** (878.3 mg, 6.0 mmol) in 88% yield.

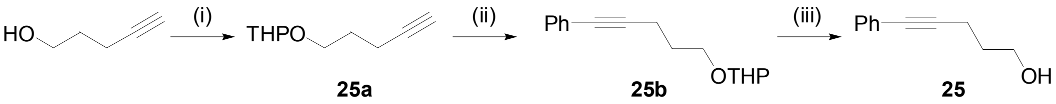
(iv) To a suspension of NaH (480 mg, 12 mmol) in THF (6 ml) was added dropwise a solution of **19c** (878.3 mg, 6.0 mmol) in THF (3 ml) at 0 °C over a period of 15 min, and then the mixture was stirred at room temperature until the evolution of hydrogen gas subsided. The mixture was cooled to 0 °C, and a solution of benzylbromide (2.052 g, 12 mmol) in THF (3 ml) was added dropwise over a period of 10 min. The mixture was allowed to warm to room temperature and stirred for 12 h. Water (5 ml) was added slowly at 0 °C, and an organic layer was separated. The aqueous layer was extracted with ether (3 x 10 ml), and the combined organic layers were washed with water (3 x 10 ml) and brine (15 ml), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica-gel (eluent; hexane/AcOEt = 10/1, R_f 0.30) to give alkyne **19** (1.35 g, 5.7 mmol) in 95% yield. Colorless oil; R_f 0.30 (hexane/AcOEt = 10/1); ^{1}H NMR ($CDCl_3$) δ 2.75 (t, J = 7.3 Hz, 2H), 3.70 (t, J = 7.3 Hz, 2H), 4.61 (s, 2H), 7.27-7.44 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 20.8, 68.4, 73.0, 81.5, 86.7, 123.6, 127.7, 128.2, 128.4, 131.6, 138.1; IR (neat) 3031 w, 2861 m, 1598 w, 1490 m, 1454 m, 1362 m, 1103 s, 1028 w, 913 w, 756 s, 693 s, 526 w; MS, m/z (relative intensity, %) 236 (5), 207 (15), 115 (31), 105 (22), 91 (100), 65 (16); exact mass calcd for 236.1201, found 236.1199.

Alkyne 21 (Table 2, entry 9). Alkyne **21** was obtained, from 4-pentyn-1-ol in place of 3-butyn-1-ol, by the same procedure as that of alkyne **19**. Colorless oil; R_f 0.44 (hexane/AcOEt = 10/1); ^{1}H NMR ($CDCl_3$) δ 1.91 (tt, J = 6.7 Hz, J = 13.4 Hz, 2H), 2.54 (t, J = 6.7 Hz, 2H), 3.64 (t, J = 6.1 Hz, 2H), 4.54 (s, 2H), 7.26-7.29 (m, 5H), 7.31-7.38 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 16.3, 28.9, 68.8, 73.0, 80.8, 89.6, 123.9, 127.5, 127.6, 128.2, 128.4, 131.5, 138.5; IR (neat) 3031 w, 2928 m, 2857 m, 2794 w, 2233 w, 1951 w, 1878 w, 1808 w, 1720 w, 1598 m, 1490 s, 1454 m, 1364 m, 1275 w, 1204 w, 1105 s, 1078 s, 1027 m, 913 w, 756 s, 737 s, 693 s, 611 w, 526 w, 456 w; MS, m/z (relative intensity, %) 250 (12), 205 (10), 159 (10), 143

(13), 131 (13), 129 (65), 128 (41), 127 (13), 117 (28), 115 (42), 105 (11), 103 (17), 92 (10), 91 (100), 77 (14), 65 (25), 51 (12); exact mass calcd for 250.1370, found 250.1364.

Alkyne 23 (Table 2, entry 10). Alkyne **23** was, from 5-hexyne-1-ol in place of 3-butyn-1-ol, obtained by the same procedure as that of alkyne **19**. Colorless oil; R_f 0.45 (hexane/AcOEt = 10/1); ^{1}H NMR (CDCl$_3$) δ 1.71 (tt, J = 7.3 Hz, J = 10.4 Hz, 2H), 1.80 (tt, J = 6.7 Hz, J = 13.4 Hz, 2H), 2.44 (t, J = 7.3 Hz, 2H), 3.53 (t, J = 6.1 Hz, 2H), 4.52 (s, 2H), 7.25-7.40 (m, 10H); ^{13}C NMR (CDCl$_3$) δ 19.2, 25.5, 29.0, 69.9, 72.9, 80.8, 90.7, 121.2, 127.5 (two overlapping signals), 127.6, 128.2, 128.4, 131.5, 138.6; IR (neat) 3031 w, 2938 m, 2861 m, 2793 w, 2232 w, 1951 w, 1877 w, 1598 w, 1490 m, 1454 m, 1442 m, 1362 m, 1309 w, 1204 w, 1108 s, 1028 m, 913 w, 756 s, 737 m, 693 s, 611 w, 526 w, 460 w, 419 w; MS. m/z (relative intensity, %) 264 (2), 173 (10), 158 (11), 156 (13), 129 (23), 128 (16), 117 (15), 115 (26), 105 (15), 91 (100), 77 (11), 65 (15); exact mass calcd for 264.1515, found 264.1515.

Alkyne 25 (Table 2, entry 11).



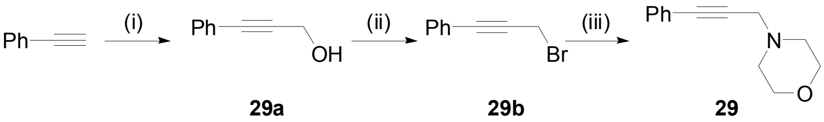
(i) To a cold (0 °C) solution of 4-pentyn-1-ol (1.68 gm 20 mmol) and p-toluenesulfonic acid (114 mg, 0.6 mmol) in ether (30 ml) was added dropwise 3,4-dihydro-2H-pyran (3.37 g, 40 mmol) over a period of 10 min, and the mixture was allowed to warm to room temperature and stirred for 12 h. The reaction mixture was poured into saturated NaHCO$_3$ aq. (10 ml), and an organic layer was separated. The aqueous layer was extracted with ether (3 x 10 ml), and the combined organic layers were dried over MgSO$_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica-gel (eluent; hexane/AcOEt = 20/1) to give **25a** (3.09 g, 18.4 mmol) in 92% yield.

(ii) A mixture of PdCl$_2$(PPh$_3$)$_2$ (280.1 mg, 0.4 mmol), PPh$_3$ (209.8 mg, 0.8 mmol), CuI (152.3 mg, 0.8 mmol), **25a** (3.365 g, 20 mmol) and Et$_2$NH (40 ml) was stirred at room temperature for 1 h and 70 °C for 48 h. Thereaction mixture was concentrated in vacuo, and the residue was purified by column chromatography on silica-gel (eluent; hexane/AcOEt = 20/1) to give **25b** (4.41 g, 18.0 mmol) in 90% yield.

(iii) A solution of p-toluenesulfonic acid (460 mg, 2.4 mmol) and **25b** (2.96 g, 12.1 mmol) in methanol (30 ml) was stirred at 70 °C for 4 d. The reaction mixture was added saturated NaHCO$_3$ aq. (10 ml), and an organic layer was separated. The aqueous layer was extracted with ether (2 x 10 ml), and the combined organic layers were concentrated in vacuo. The residue was purified by column chromatography on silica-gel (hexane/AcOEt = 4/1, R_f 0.12) to give alkyne **25** (1.94 g, 20 mmol) in 100% yield. Colorless oil; *Rf* 0.12 (eluent; hexane/AcOEt = 4/1); ^{1}H NMR ($CDCl_3$) δ 1.85 (tt, *J* = 6.7 Hz, *J* = 7.3 Hz, 2H), 1.97 (bs, 1H), 2.53 (t, *J* = 7.3 Hz, 2H), 3.80 (t, *J* = 6.8 Hz, 2H), 7.25-7.30 (m, 3H), 7.36-7.41 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 15.9, 31.3, 61.6, 81.1, 89.3, 123.6, 127.6, 128.2, 131.5; IR (neat) 3302 m, 3056 m, 2946 m, 2233 w, 1952 w, 1880 w, 1806 w, 1663 w, 1598 m, 1571 w, 1490 s, 1467 m, 1442 s, 1430 s, 1381 m, 1349 m, 1327 m, 1176 w, 1059 m, 960 w, 915 m, 757 m, 693 w; MS, m/z (relative intensity, %) 174 (19), 160 (16), 159 (100); exact mass calcd for 160.0888, found 160.0882.

Alkyne 27 (Table 2, entry 12). Alkyne **27** was obtained, from 5-hexyne-1-ol in place of 4-pentyn-1-ol, by the same procedure as that of alkyne **25**. Colorless oil; *Rf* 0.10 (hexane/AcOEt = 4/1); ^{1}H NMR ($CDCl_3$) δ 1.64-1.78 (m, 4H, 4 and 5-H), 2.04 (bs, 1H, O*H*), 2.44 (t, *J* = 6.7 Hz, 2H, 3-H), 3.68 (t, *J* = 6.1 Hz, 2H, 6-H), 7.24-7.29 (m, 3H, Ph), 7.36-7.41 (m, 2H, Ph); ^{13}C NMR ($CDCl_3$) δ 19.1 (3-C), 24.9 (4-C), 31.8 (5-C), 62.3 (6-C), 80.9 (1-C), 89.8 (2-C), 123.8 (Ph), 127.5 (Ph), 128.1 (Ph), 131.5 (Ph); IR (neat) 3302 m, 3057 m, 2938 m, 2232 w, 1952 w, 1881 w, 1723 w, 1691 w, 1664 w, 1598 s, 1572 w, 1492 s, 1442 s, 1433 m, 1412 m, 1368 m, 1331 m, 1159 w, 1063 m, 990 w, 915 w, 757 m, 693 m, 526 w; MS, m/z (relative intensity, %) 174 (21), 146 (14), 145 (14), 141 (17), 131 (14), 130 (80), 129 (46), 128 (64), 127 (13), 118 (14), 117 (40), 116 (16), 115 (100), 102 (14), 91 (23), 89 (15), 63 (11); exact mass calcd for 174.1045, found 174.1044.

Alkyne 29 (Table 2, entry 13).

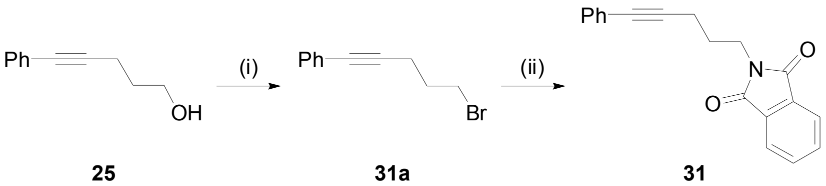


(i) To a mixture of ethylGrignard reagent (31.1 g, 233 mmol) in THF (150 ml) was added dropwise ethynylbenzene (20.4 g, 200 mmol) over a period of 30 min at 10 °C, and then the mixture was stirred at room temperature until the evolution of ethane gas subsided. Paraformaldehyde (8.00 g, 233 mmol) was added portionwise to the mixture over a period of 15 min at 10 °C, and the mixture was stirred at 70 °C for 14 h. 2*N* HCl aqueous (150 ml) was added the mixture, and an organic layer was separated. The aqueous layer was extracted with ether (3 x 60 ml), and the combined organic layers were washed with saturated $NaHCO_3$ aq. (3 x 30 ml) and brine (30 ml), dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by distillation under reduced pressure (bp. 116 °C/4.8 mmHg) to give **29a** (23.0 g, 174 mmol) in 87% yield.

(ii) To a cold (-40 °C) solution of **29a** (13.2 g, 100 mmol) and pyridine (0.5 ml, 6.0 mmol) in ether (30 ml) was added dropwise PBr_3 (4.3 ml, 45 mmol) over a period of 15 min, and the mixture was stirred for 30 min. The mixture was allowed to warm to -20 °C, and stirred for 1 h, 1h at 0 °C and 1 h at room temperature. Brine (50 ml) was added slowly at 0 °C, and an organic layer was separated. The aqueous layer was extracted with ether (3 x 20 ml), and the combined organic layers were washed with water (2 x 20 ml), saturated $NaHCO_3$ aq. (2 x 20 ml) and brine (2 x 20 ml), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica-gel (eluent; hexane, R_f 0.20) to give **29b** (17.9 g, 91.8 mmol) in 92% yield.

(iii) To a mixture of K_2CO_3 (1.38 g, 10 mmol) and **29b** (975.3 mg, 5 mmol) in CH_3CN (10 ml) was added morpholine (522.7 mg, 6 mmol) slowly, and the mixture was stirred at room temperature for 12 h. The reaction mixture was filtered and concentrated in vacuo. The residue was diluted with ether (20 ml), water (10 ml) was added, and an organic layer was separated. The aqueous layer was extracted with ether (2 x 10 ml), and the combined organic layers were washed with water (2 x 15 ml) and brine (15 ml), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica-gel (eluent; hexane/AcOEt = 2/1, R_f 0.12) to give alkyne **29** (599.1 mg, 2.98 mmol) in 60% yield. Colorless oil; R_f 0.12 (hexane/AcOEt = 2/1); ^1H NMR ($CDCl_3$) δ 2.64 (t, J = 4.3 Hz, 4H, CH_2), 3,51 (s, 2H, 3-H), 3.77 (t, J = 4.3 Hz, 4H, CH_2), 7.28-7.44 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ 48.0 (3-C), 52.4 ($\mathit{C}H_2$), 66.8 ($\mathit{C}H_2$), 83.9 (1-C), 85.6 (2-C), 122.9 (Ph), 128.1 (Ph), 128.2 (Ph), 131.7 (Ph); IR (neat) 3056 w, 2909 m, 2855 m, 2813 m, 2761 m, 2692 w, 1972 w, 1710 w, 1678 w, 1599 m, 1492 s, 1461 m, 1453 s, 1442 s, 1393 m, 1346 s, 1333 s, 1289 s, 1269 m, 1238 m, 1206 w, 1117 s, 1072 m, 1006 m, 912 w, 862 m, 758 m, 693 m, 563 w, 526 w; MS, m/z (relative intensity, %) 202 (27), 201 (91), 200 (67), 172 (23), 171 (73), 170 (80), 157 (14), 156 (66), 144 (26), 143 (71), 142 (40), 141 (12), 130 (12), 129 (39), 128 (62), 117 (30), 116 (64), 115 (100), 114 (28), 113 (17), 103 (10), 94 (13), 89 (51), 88 (14), 87 (11), 86 (64), 75 (11), 65 (23), 63 (34), 62 (10), 56 (56), 54 (11); exact mass calcd for 201.1153, found 201.1154.

Alkyne 31 (Table 2, entry 14).



(i) To a cold (0 °C) solution of CBr_4 (3.32 g, 10 mmol) and **25** (1.22 g, 7.6 mmol) in CH_2Cl_2 (15 ml) was added portionwise PPh_3 (2.36 g, 9 mmol) over a period of 15 min, and the mixture was stirred at room temperature for 12 h. The reaction mixture was poured into saturated $NaHCO_3$ aq. (30 ml), and an organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (3 x 20 ml), and combined organic layers were washed with brine (2 x 10 ml), dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica-gel (eluent; hexane/AcOEt = 100/1) to give **31a** (1.65 g, 7.37 mmol) in 97% yield.

(ii) A solution of **31a** (1.09 g, 4.9 mmol) and phthalimide (1.11 g, 6 mmol) in DMF (10 ml) was stirred at room temperature for 24 h. To the reaction mixture was added ether (50 ml) and water (10 ml), and the organic layer was separated. The aqueous layer was extracted with ether (3 x 20 ml), and the combined organic layers were washed with water (2 x 10 ml) and brine (15 ml), dried over $MgSO_4$, and concentrated in vacuo. Washing of the solid residue with hexane gave alkyne **31** (1.01 g, 3.49 mmol) in spectroscopically pure form in 71% yield. White solid; mp 125-127 °C (hexane/AcOEt = 4/1); R_f 0.23 (hexane/AcOEt = 4/1); ^{1}H NMR ($CDCl_3$) δ 2.02 (tt, J = 6.7 Hz, J = 7.4 Hz, 2H, 4-H), 2.50 (t, J = 6.7 Hz, 2H, 3-H), 3.87 (t, J = 7.4 Hz, 2H, 5-H), 7.20-7.30 (m, 5H, Ph), 7.65-7.88 (m, 4H, Ph); ^{13}C NMR ($CDCl_3$) δ 17.3 (3-C), 27.3 (4-C), 37.4 (5-C), 81.2 (1-C), 88.7 (2-C), 123.2 (Ph), 123.6 (Ph), 127.5 (Ph), 128.0 (Ph), 128.9 (Ph), 131.5 (Ph), 133.8 (Ph), 168.4 (two overlapping signals, *C*O); IR (KBr) 1776 m, 1756 m, 1710 s, 1699 m, 1600 w, 1493 w, 1469 w, 1433 m, 1402 s, 1373 s, 1341 m, 1308 w, 1191 w, 1118 w, 1027 m, 759 w, 723 m, 691 w; MS, m/z (relative intensity, %) 290 (38), 289 (88), 288 (20), 270 (10), 260 (13), 244 (14), 198 (11), 184 (53), 171 (22), 161 (81), 160 (85), 148 (16), 143 (47), 142 (100), 141 (85), 133 (31), 132 (23), 130 (34), 129 (37), 128 (43), 127 (15), 117 (16), 116 (12), 115 (67), 105 (42), 104 (36), 102 (21), 89 (11), 77 (34), 76 (25); exact mass calcd for 289.1103, found 289.1104.

Typical Procedure for Cyclohydrocarbonylation of Alkynes with Formaldehyde in Aqueous Media; condition A: In a 10-ml screw-capped vial were placed $[RhCl(cod)]_2$ (6.16 mg, 0.0125 mmol), dppp (10.31 mg 0.025 mmol), TPPTS (14.21 mg, 0.025 mmol) and water (0.5 ml), and the mixture was stirred at room temperature for 15 min and turned out to a light yellow suspension. After SDS (144.2 mg, 0.5 mmol), formalin (0.06 ml, 0.75 mmol), Alkyne (0.25 mmol) and water (1.44 ml) were added, the mixture was degassed, charged with N_2, and stirred at 100 °C for 15 h. Ether (10 ml) was added to the reaction mixture, and the biphasic mixture was stirred for 15 min. The separated aqueous layer was extracted with ether (3 x 10 ml), and the combined organic layers were dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography to give butenolide **2**.

Typical Procedure for Cyclocarbonylation of Alkynes with Paraformaldehyde in Xylene; condition B: In a 10-ml screw-capped vial were placed $[RhCl(cod)]_2$ (6.16 mg, 0.0125 mmol), dppp (10.31 mg, 0.025 mmol) and xylene (0.5 ml), and the mixture was stirred at room temperature for 15 min and turned out to a light yellow suspension. After paraformaldehyde (37.54 mg, 1.25 mmol), alkyne (0.25 mmol) and xylene (1.5 ml) were added the mixture was degassed, charged with N_2, and stirred at 100 °C for 24 h. The reaction mixture was concentrated *in vacuo*. The residue was purified by column chromatography on silica-gel to give butenolide **2**.

Procedure for Cyclocarbonylation of Alkynes with Carbon Monoxide (Table 1, entry 2). In a 10-ml screw-capped vial equipped with 1 L of gas bag were placed $[RhCl(cod)]_2$ (6.16 mg, 0.0125 mmol), dppp (10.31 mg, 0.025 mmol) and xylene (0.5 ml), and the mixture was stirred at room temperature for 15 min and turned out to a light yellow suspension. After alkyne **1** (0.25 mmol) and xylene (1.5 ml) was added the mixture was degassed, charged with 1 atm of carbon monoxide and stirred at 100 °C for 24 h. The reaction mixture was concentrated *in vacuo*. The residue was purified by column chromatography on silica-gel to give recovered alkyne **1** in 84% yield.

Procedure for Cyclocarbonylation of Alkynes with Synthesis Gas (Table 1, entry 4). In a 10-ml screw-capped vial equipped with 1 L of gas bag were placed $[RhCl(cod)]_2$ (6.16 mg, 0.0125 mmol), dppp (10.31 mg 0.025 mmol), TPPTS (14.21 mg, 0.025 mmol) and water (0.5 ml), and the mixture was stirred at room temperature for 15 min and turned out to a light yellow suspension. After SDS (144.2 mg, 0.5 mmol), alkyne **1** (0.25 mmol) and water (1.44 ml) were added, the mixture was degassed, charged with 1 atm of synthesis gas and stirred at 100 °C for 24 h. Ether (10 ml) was added to the reaction mixture, and the biphasic mixture was stirred for 15 min. The separated aqueous layer was extracted with ether (3 x 10 ml), and the combined organic layers were dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica-gel to give butenolide **2** and recovered alkyne **1** in 6% yield and 68% yield.

Butenolide 2. White solid; mp 89-93 °C (hexane/ether = 5/1); ^{1}H NMR ($CDCl_3$) δ 5.15 (s, 2H), 7.29-7.43 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 70.4, 125.9, 127.3, 128.5, 128.6, 128.8, 129.1, 130.0, 130.5, 130.6, 156.1, 173.3; IR (KBr) 3856 w, 3753 w, 3651 w, 3470 w, 3058 w, 2925 w, 2367 w, 1911 w, 1847 w, 1739 s, 1639 m, 1574 m, 1543 w, 1487 m, 1442 m, 1365 m, 1341 s, 1226 w, 1162 m, 1083 m, 1063 m, 1036 m, 1000 w, 958 m, 920 w, 788 m, 774 m, 760 m, 741 m, 695 s, 612 m, 503 m, 470 w; MS, m/z (relative intensity, %) 237 (12), 236 (73), 207 (13), 180 (15), 179 (100), 178 (62), 176 (12), 152 (10), 131 (25), 105 (58), 95 (14), 94 (22), 89 (21), 82 (21), 77 (14), 76 (21), 63 (13), 51 (18); exact mass calcd for 236.0837, found 236.0835.

Butenolide 4 (Eq 3). White solid; mp 69-70 °C (hexane/AcOEt = 2/1); ^{1}H NMR ($CDCl_3$) δ 5.32 (s, 2H, 5-H), 7.50 (t, *J* = 7.9 Hz, 1H, Ph), 7.53 (t, *J* = 7.3 Hz, 1H, Ph), 7.68 (tt, *J* = 1.2 Hz, *J* = 7.3 Hz, 1H, 4b-H), 7.91 (d, *J* = 7.9 Hz, 1H, Ph); ^{13}C NMR ($CDCl_3$) δ 69.6 (5-C), 122.1 (3b-C), 125.7 (4a-C), 129.0 (two overlapping signals, 3-C, 3a-C), 134.0 (4b-C), 146.5 (4-C), 171.1 (2-C); IR (KBr): 1777 s, 1754 s, 1596 w, 1468 m, 1440 m, 1369 m, 1318 m, 1219 m, 1052 m, 1018 w, 1001 m, 740 w; MS, m/z (relative intensity, %) 135 (16), 134 (75), 133 (45), 106 (36), 105 (100), 104 (14), 89 (16), 78 (19), 77 (77), 76 (40), 75 (20), 74 (25), 63 (24), 62 (12), 51 (41); exact mass calcd for 134.0368, found 134.0369.

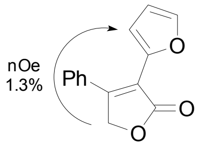
Butenolide 6 (Table 2, entry 1). Colorless oil; R_f 0.20 (hexane/AcOEt = 4/1); ^{1}H NMR ($CDCl_3$) δ 0.92 (t, *J* = 7.9 Hz, 3H), 0.98 (t, *J* = 7.3 Hz, 3H), 1.48-1.59 (m, 4H), 2.23 (t, *J* = 7.9 Hz, 2H), 2.39 (t, *J*= 7.9 Hz, 2H), 4.65 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 13.9, 14.0, 21.3, 21.4, 31.9, 32.8, 71.1, 127.0, 160.6, 175.2; IR (neat) 3483 w, 2960 s, 2927 s, 2872 m, 2855 m, 1754 s, 1670 w, 1464 w, 1379 w, 1347 w, 1233 w, 1347 w, 1233 w, 1177 w, 1094 m, 1057 m, 1038 m, 957 w, 811 w, 787 w, 763 w, 419 w; MS, m/z (relative intensity, %) 169 (11), 168 (92), 154 (10), 153 (100), 140 (24), 139 (37), 125 (33), 112 (12), 111 (16), 107 (11), 95 (13), 93 (17), 81 (15), 79 (14), 69 (44), 67 (16), 55 (26), 53 (10); exact mass calcd for 168.1150, found 168.1153.

Butenolide 12 (Table 2, entry 4). GC analysis of the crude reaction mixture showed that a mixture of major-**12** and minor-**12** were produced in a ratio of 66/34. Both isomers can be separated easily by column chromatography on silica-gel (eluent; hexane/AcOEt = 2/1). Spectral data of both major-**12** and minor-**12** were accorded with those in the previous report.[2]
(major-**12**): Colorless oil; R_f 0.24 (hexane/AcOEt = 2/1); ^{1}H NMR ($CDCl_3$) δ 2.22 (s, 3H), 4.79 (s, 2H), 7.36-7.50 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 13.4, 72.4, 126.7, 128.4, 128.5, 128.8, 129.8, 157.6, 173.3; IR (neat) 3488 w, 3057 w, 2925 w, 2857 w, 1802 w, 1760 s, 1740 s, 1661 w, 1496 w, 1444 m, 1385 m, 1333 m, 1230 m, 1129 s, 1061 m, 1015 m, 964 s, 918 w, 790 s, 741 m, 700 s, 617 w, 553 m, 421 w; MS, m/z (relative intensity, %) 174 (61), 146 (10), 145 (19), 131 (10), 118 (10), 117 (100), 115 (40), 91 (13); exact mass cald for 174.0681, found 174.0683.
(minor-**12**): Colorless crystal; mp 110-113 °C (hexane/CH_2Cl_2 = 10/1); R_f 0.35 (hexane/AcOEt = 2/1); ^{1}H NMR ($CDCl_3$) δ 2.14 (t, *J* = 1.8 Hz, 3H), 5.06 (q, *J* = 1.8 Hz, 2H), 7.40-7.55 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 10.4, 70.5, 123.0, 127.2, 129.1, 130.2, 131.4, 154.8, 175.9; IR (KBr) 3856 w, 3753 w, 3652 w, 3570 w, 2927 w, 2346 w, 1738 s, 1649 w, 1560 w, 1499 w, 1451 w, 1344 w, 1231 w, 1091 m, 1046 m, 977 w, 767 m, 694 m, 610 w, 452 w, 411 w; MS, m/z (relative intensity) 175 (12), 174 (96), 146 (12), 145 (100), 129 (11), 117 (83), 116 (18), 115 (64), 91 (15); exact mass calcd for 174.0681, found 174.0681.

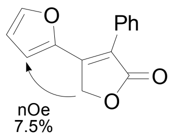
Butenolide 14 (Table 2, entry 5). GC analysis of the crude reaction mixture showed that a mixture of major-**14** and minor-**14** were produced in a ratio of 96/4. Both isomers can be separated easily by column chromatography on silica-gel (eluent; hexane/AcOEt = 2/1). Spectral data of both major-**14** and minor-**14** were accorded with those in the previous report.[2]
(major-**14**): Colorless crystal; mp 139-144 °C (hexane/CH_2Cl_2 = 5/1); R_f 0.24 (hexane/AcOEt = 2/1); ^1H NMR ($CDCl_3$) δ 5.18 (s, 2H), 7.36-7.44 (m, 7H), 7.62-7.66 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 70.2, 114.0, 128.1, 129.0, 129.1, 129.5, 132.7, 135.3, 153.3, 189.4; IR (KBr) 3856 w, 3753 w, 3651 w, 3569 w, 3051 w, 2925 w, 2230 m, 1750 s, 1655 w, 1608 w, 1509 w, 1444 w, 1345 m, 1161 m, 1063 m, 1037 m, 959 w, 842 m, 787 m, 743 w, 698 m, 666 w, 591 w, 545 m, 426 w; MS, m/z (relative intensity, %) 261 (60), 232 (13), 205 (17), 204 (100), 203 (27), 177 (10), 176 (10), 131 (18); exact mass calcd for 261.0790, found 261.0789.
(minor-**14**): Colorless crystal; mp 143-145 °C (hexane/CH_2Cl_2 = 5/1); R_f 0.24 (hexane/AcOEt = 2/1); ^1H NMR ($CDCl_3$) δ 5.21 (s, 2H), 7.26-7.29 (m, 2H), 7.37-7.42 (m, 2H), 7.44-7.48 (m, 1H), 7.56-7.59 (m, 2H), 7.65-7.68 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 70.8, 112.5, 124.5, 127.4, 129.4, 130.1 (two overlapping signals), 131.2, 132.4, 134.9, 158.7, 178.9; IR (KBr) 3856 w, 3753 w, 3651 w, 3483 w, 3055 w, 2925 w, 2225 m, 1749 s, 1644 m, 1605 w, 1445 m, 1345 m, 1230 w, 1157 m, 1068 m, 1039 m, 958 m, 893 w, 851 m, 762 m, 698 m, 592 w, 466 w, 404 w; MS, m/z (relative intensity, %) 261 (69), 232 (24), 205 (17), 204 (100), 203 (32), 177 (12), 176 (12), 105 (37); exact mass calcd for 261.0790, found 261.0786.

Butenolide 16 (Table 2, entry 6). GC analysis of the crude reaction mixture showed that a mixture of major-**16** and minor-**16** were produced in a ratio of 52/48. Both regio isomers were not separatable, spectral data was obtained in the mixture (major-**16**/minor-**16**): Spectral data of both major-**16** and minor-**16** were accorded with those in the previous report.[2] Colorless oil: R_f 0.37 (hexane/AcOEt = 2/1). ^1H NMR ($CDCl_3$) major: δ 3.82 (s, 3H), 5.15 (s, 2H), 6.84 (dd, J = 2.4 Hz, J = 9.2 Hz, 2H), 7.26-7.44 (m, 7H); minor: δ 3.83 (s, 3H), 5.17 (s, 2H), 6.90 (dd, J = 2.4 Hz, J = 9.2 Hz, 2H), 7.26-7.44 (m, 7H); ^{13}C NMR ($CDCl_3$) (major-**16**/minor-**16**): δ 55.3, 55.4, 70.6, 91.8, 114.1, 114.4, 122.3, 127.4, 128.7, 129.0, 129.1, 129.3, 130.4, 130.6, 135.0 (two overlapping signals), 160.0 (two overlapping signals), 178.4 (two overlapping signals); IR (neat) (major-**16**/minor-**16**): 2925 m, 2853 w, 1747 s, 1641 w, 1606 m, 1573 w, 1515 m, 1445 m, 1366 m, 1340 m, 1295 m, 1253 m, 1179 m, 1159 m, 1113 w, 1065 m, 1029 m, 958 m, 834 m, 789 w, 765 m, 697 m, 589 w, 526 w; MS, m/z (relative intensity, %) (major-**16**): 266 (100), 237 (14), 210 (15), 209 (82), 194 (14), 178 (18), 166 (11), 165 (32), 135 (32), 133 (14); exact mass calcd for 266.0943, found 266.0949; (minor-**16**): 266 (100), 238 (13), 210 (16), 209 (83), 194 (14), 178 (17), 166 (10), 165 (29), 161 (20), 133 (26), 105 (18); exact mass calcd for 266.0943, found 266.0944.

Butenolide 18 (Table 2, entry 7). GC analysis of the crude reaction mixture showed that a mixture of major-**18** and minor-**18** were produced in a ratio of 58/42. Both isomers can be separated easily by column chromatography on silica-gel (eluent; hexane/AcOEt = 4/1, *R_f* 0.17). (major-**18**): White solid; mp 154-157 °C (hexane/AcOEt = 1/1); R_f 0.17 (hexane/AcOEt = 4/1); ^{1}H NMR ($CDCl_3$) δ 5.21 (s, 2H), 6.46 (dd, J = 1.8 Hz, J = 3.7 Hz, 1H), 6.73 (d, J = 3.7 Hz, 1H), 7.39-7.55 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 68.6, 112.4, 113.9, 122.4, 128.5, 129.0, 129.1, 130.1, 144.9, 145.0, 146.2, 173.3; IR (KBr): 3854 w, 3745 w, 3630 w, 3138 w, 1746 s, 1697 w, 1647 m, 1600 w, 1478 m, 1437 w, 1337 m, 1219 w, 1173 w, 1092 m, 1066 m, 1037 m, 941 w, 771 m, 703 m, 664 w; MS, m/z (relative intensity, %);
(minor-**18**): White solid; mp 104-108 °C (hexane/AcOEt = 1/1); R_f 0.29 (hexane/AcOEt = 4/1); ^{1}H NMR ($CDCl_3$) δ 5.12 (s, 2H), 6.50 (dd, J = 1.8 Hz, J = 3.7 Hz), 7.23 (d, J = 3.7 Hz, 1H), 7.39 (d, J = 1.8 Hz, 1H), 7.43-7.54 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 71.2, 111.5, 112.8, 119.4, 127.9, 128.6, 130.4, 131.2, 143.0, 145.5, 152.6, 171.5; IR (KBr): 3855 w, 3745 w, 3630 w, 3569 w, 1752 s, 1701 w, 1654 w, 1560 w, 1443 w, 1341 m, 1139 m, 1065 m, 1040 m, 1015 m, 970 m, 872 w, 748 m, 696 m 452 w; MS, m/z (relative intensity, %) 227 (48), 226 (100), 199 (17), 198 (96), 197 (20), 170 (38), 169 (97)153 (21), 152 (34), 151 (13), 142 (31), 141 (97), 140 (12), 139 (50), 121 (22), 115 (81), 113 (12), 105 (97), 102 (11), 91 (12), 77 (15), 76 (20), 75 (11), 63 (15), 51 (13); exact mass calcd for 226.0630, found 226.0628.



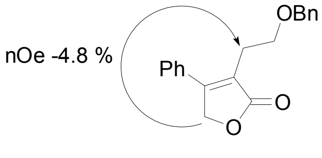
major-**18**



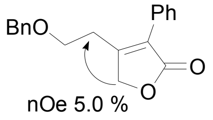
minor-**18**

Butenolide 20 (Table 2, entry 8). GC analysis of the crude reaction mixture showed that a mixture of major-**8** and minor-**8** were produced in a ratio of 74/26. Both isomers can be separated easily by column chromatography on silica-gel (eluent; hexane/AcOEt = 4/1). (major-**20**): Colorless crystal; mp 74-77 °C (hexane/CH_2Cl_2 = 10/1); R_f 0.13 (hexane/AcOEt = 4/1); ^{1}H NMR ($CDCl_3$) δ 2.84 (t, J = 6.7 Hz, 2H), 3.80 (t, J = 6.7 Hz, 2H), 4.51 (s, 2H), 5.04 (s, 2H), 7.26-7.57 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 25.4, 67.5, 70.9, 73.0, 124.3, 127.4, 127.5 (two overlapping signals), 128.3, 129.1, 130.3, 131.2, 138.2, 154.9, 165.9; IR (KBr) 3856 w, 3753 w, 3651 w, 3570 w, 3057 w, 2856 w, 1744 s, 1656 m, 1449 w, 1356 w, 1242 w, 1097 m, 1052 w, 1011 w, 965 w, 923 w, 743 m, 692 m, 631 w, 445 w; MS, m/z, relative intensity, %) 294 (0.3), 203 (12), 188 (62), 187 (40), 129 (10), 91 (100); exact mass calcd for 294.1256, found 294.1255.

(minor-**20**): Colorless oil: R_f 0.06 (hexane/AcOEt = 4/1); ^{1}H NMR ($CDCl_3$) δ 2.89 (t, *J* = 6.1 Hz, 2H), 3.66 (t, *J* = 6.1 Hz, 2H), 4.52 (s, 2H), 4.89 (s, 2H), 7.28-7.47 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 28.5, 67.4, 72.0, 73.3, 127.7, 128.0, 128.5 (two overlapping signals), 128.6, 128.9, 129.0 (two overlapping signals), 129.8, 159.8, 173.3; IR (neat) 3030 w, 2925 m, 2856 m, 1757 s, 1660 w, 1496 w, 1446 w, 1361 w, 1308 w, 1259 w, 1179 w, 1130 m, 1099 m, 1041 m, 985 w, 790 m, 740 m, 699 m, 674 w, 611 w, 544 w; MS, m/z (relative intensity, %) 294 (9) 203 (10), 175 (10), 91 (100); 294.1256, found 294.1255.



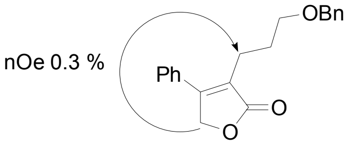
major-**20**



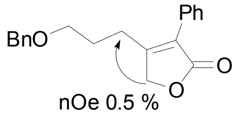
minor-**20**

Butenolide 22 (Table 2, entry 9). GC analysis of the crude reaction mixture showed that a mixture of major-**22** and minor-**22** were produced in a ratio of 81/19. Both isomers can be separated easily by column chromatography on silica-gel (eluent; hexane/AcOEt = 2/1). (major-**22**): Colorless oil; R_f 0.35 (hexane/AcOEt = 2/1); ^{1}H NMR ($CDCl_3$) δ 1.96 (tt, *J* = 6.1 Hz, *J* = 7.3 Hz, 2H), 2.69 (t, *J* = 7.3 Hz, 2H), 3.54 (t, *J* = 6.1 Hz, 2H), 4.46 (s, 2H), 5.03 (s, 2H), 7.27-7.36 (m, 5H), 7.39-7.48 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 21.4, 27.8, 69.5, 70.6, 72.8, 127.0, 127.2, 127.5 (two overlapping signals), 128.3, 129.2, 130.2, 131.3, 138.5, 155.5, 175.1; IR (neat) 3483 w, 3061 w, 3030 w, 2926 s, 2857 s, 2794 w, 1956 w, 1747 s, 1646 m, 1576 w, 1496 m, 1453 s, 1362 m, 1345 s, 1280 w, 1176 m, 1094 s, 1073 s, 1055 s, 1030 m, 914 w, 851 w, 766 s, 738 m, 696 s, 646 w, 462 w; MS, m/z (relative intensity, %) 308 (1), 217 (41), 203 (15), 202 (100), 201 (47), 174 (46), 157 (10), 145 (13), 130 (19), 129 (40), 128 (17), 117 (11), 115 (18), 91 (83), 77 (10), 65 (12); exact mass calcd for 308.1412, found 308.1421.

(minor-**22**): Colorless oil; R_f 0.24 (hexane/AcOEt = 2/1); ^{1}H NMR ($CDCl_3$) δ 1.92 (tt, *J* = 6.1 Hz, *J* = 7.9 Hz, 2H), 2.81 (t, *J* = 7.9 Hz, 2H), 3.55 (t, *J* = 6.1 Hz, 2H), 4.51 (s, 2H), 4.89 (s, 2H), 7.33-7.53 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 24.7, 27.9, 69.1, 71.2, 73.1, 126.8, 127.6, 128.4, 128.5, 128.5, 128.9, 129.1, 129.9, 138.0, 161.6, 173.5; IR (neat) 3483 w, 3060 w, 2920 m, 2859 m, 1795 w, 1757 s, 1658 w, 1496 m, 1445 m, 1362 m, 1308 w, 1205 w, 1128 m, 1103 m, 1038 m, 953 m, 914 w, 790 m, 740 m, 698 m, 611 w, 553 w, 418 w; MS, m/z (relative intensity, %) 308 (17), 217 (22), 199 (11), 129 (11), 115 (12), 91 (100); exact mass calcd for 308.1412, found 308.1412.



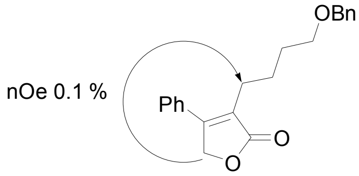
major-**22**



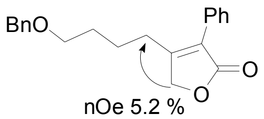
minor-**22**

Butenolide 24 (Table 2, entry 10). GC analysis of the crude reaction mixture showed that a mixture of major-**24** and minor-**24** were produced in a ratio of 56/44. Both isomers can be separated easily by column chromatography on silica-gel (eluent; hexane/AcOEt = 4/1). (major-**24**): Colorless oil; R_f 0.12 (hexane/AcOEt = 4/1); ^{1}H NMR ($CDCl_3$) δ 1.65-1.76 (m, 4H), 2.56 (t, *J* = 6.7 Hz, 2H), 3.49 (t, *J* = 6.1 Hz, 2H), 4.49 (s, 2H), 5.03 (s, 2H), 7.28-7.43 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 24.2 (CH_2), 24.5 (CH_2), 29.6 (CH_2), 69.8 (CH_2), 70.6 (5-C), 72.9 (Bn-CH_2), 127.1 (3-C), 127.4 (Ph), 127.5 (Ph), 127.6 (Ph), 128.3 (Ph), 129.2 (Ph), 130.1 (Ph), 131.3 (Ph), 138.5 (Ph), 155.4 (4-C), 175.0 (2-C); IR (neat) 3483 w, 3060 m, 3030 m, 1956 w, 1747 s, 1651 m, 1576 w, 1496 m, 1454 s, 1366 m, 1345 m, 1206 w, 1099 s, 1053 m, 1017 m, 913 w, 766 m, 738 m, 697 s, 644 w, 462 w; MS, m/z (relative intensity, %) 322 (4), 231 (53), 216 (46), 213 (11), 199 (11), 175 (11), 171 (11), 143 (11), 129 (21), 128 (13), 117 (10), 115 (17), 105 (15), 92 (10), 91 (100), 65 (10); exact mass calcd for 322.1569, found 322.1562.

(minor-**24**): Colorless oil; R_f 0.06 (hexane/AcOEt = 4/1); ^{1}H NMR ($CDCl_3$) δ 1.60-1.71 (m, 4H, CH_2), 2.63 (t, *J* =7.3 Hz, 2H), 3.45 (t, *J* = 5.5 Hz, 2H), 4.47 (s, 2H), 4.83 (s, 2H), 7.27-7.44 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 24.7, 27.5, 29.6, 69.3, 71.1, 73.0, 126.7, 127.6, 127.7, 128.4, 128.5 (two overlapping signals), 128.9, 129.9, 138.3, 161.8, 173.5; IR (neat) 3030 w, 2927 m, 2859 m, 1757 s, 1658 w, 1496 m, 1454 m, 1362 w, 1128 m, 1035 m, 957 w, 790 m, 740 m, 698 m, 609 w, 416 w; MS, m/z (relativeintensity, %) 322 (25), 231 (21), 115 (11), 91 (100); exact mass calcd for 322.1569, found 322.1561.



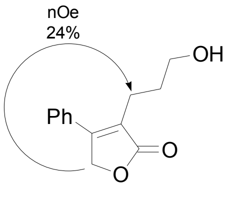
major-**24**



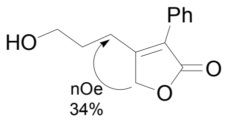
minor-**24**

Butenolide 26 (Table 2, entry 11). GC analysis of the crude reaction mixture showed that a mixture of major-**26** and minor-**26** were produced in a ratio of 63/37. Recycling preparative HPLC can separate both isomers. (major-**26**): Colorless oil; R_f 0.07 (hexane/AcOEt = 1/1); ^{1}H NMR ($CDCl_3$) δ 1.78 (m, 3H), 2.71 (t, *J* = 7.3 Hz, 2H), 3.64 (t, *J* = 6.2 Hz, 2H), 4.84

(s, 2H), 7.34-7.46 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 20.4, 31.0, 61.4, 70.9, 126.9, 127.2, 129.2, 130.4, 131.1, 156.1, 175.9; IR (neat): 3408 w, 2931 w, 1754 s, 1725 s, 1711 w, 1657 w, 1600 w, 1494 w, 1443 m, 1345 m, 1132 m, 1062 w, 955 w, 791 w, 701 w; MS, m/z (relative intensity, %): (minor-**26**): Colorless crystal; mp 44-47 °C (hexane/AcOEt = 2/1) R_f 0.15 (hexane/AcOEt = 1/1); ^{1}H NMR ($CDCl_3$) δ 1.87 (tt, J = 6.2 Hz, J = 7.9 Hz, 2H), 2.11 (s, 1H), 2.67 (t, J = 7.3 Hz, 2H), 3.67 (t, J = 6.1 Hz, 2H), 5.08 (s, 2H), 7.44-7.51 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 24.2, 30.4, 61.7, 71.2, 126.8, 128.5, 128.8, 129.8, 161.8, 173.6; IR (KBr): 3250 w, 2948 w, 1721 s, 1712 s, 1692 w, 1639 m, 1502 w, 1448 m, 1348 m, 1164 m, 1066 w, 1011 w, 768 w, 691 w; MS, m/z (relative intensity, %) 218 (19), 200 (58), 188 (28), 187 (43), 174 (63), 173 (33), 172 (11), 157 (12), 156 (16), 155 (49), 154 (12), 145 (10), 144 (11), 143 (41), 142 (15), 141 (38), 131 (15), 130 (36), 129 (100), 128 (77), 127 (24), 117 (29), 116 (20), 115 (76), 105 (14), 103 (16), 102 (14), 91 (48), 89 (10), 78 (12), 77 (27), 65 (13), 63 (12), 51 (15); exact mass calcd for 218.0943, found 218.0946.



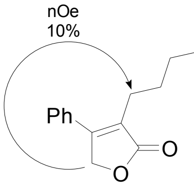
major-**26**



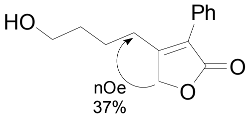
minor-**26**

Butenolide 28 (Table 2, entry 12). GC analysis of the crude reaction mixture showed that a mixture of major-**28** and minor-**28** were produced in a ratio of 54/46. Recycling preparative HPLC can separate both isomers. (major-**28**): Colorless oil; R_f 0.07 (hexane/AcOEt = 1/1); ^{1}H NMR ($CDCl_3$) δ 1.54-1.68 (m, 4H), 1.87 (bs, 1H), 2.63 (t, J = 7.3 Hz, 2H), 3.61 (t, J = 6.1 Hz, 2H), 4.83 (s, 2H), 7.34-7.45 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 24.2, 27.4, 32.2, 61.9, 71.1, 126.7, 128.5, 128.5, 128.8, 129.9, 161.9, 173.6; IR (neat): 3408 w, 2935 w, 2867 w, 1754 s, 1727 s, 1658 w, 1600 w, 1494 w, 1445 m, 1343 w, 1131 m, 1031 w, 791 w, 700 w; MS, m/z (relative intensity, %):

(minor-**28**): Colorless oil; R_f 0.18 (hexane/AcOEt = 1/1); ^{1}H NMR ($CDCl_3$) δ 1.59-1.73 (m, 4H), 2.56 (t, J = 7.3 Hz, 2H), 3.66 (t, J = 6.1 Hz, 2H), 5.03 (t, J = 6.1 Hz, 2H), 7.40-7.51 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 24.0, 24.1, 32.3, 62.3, 70.7, 127.1, 127.4, 129.2, 130.2, 131.3, 155.6, 175.2; IR (neat): 3496 w, 2922 w, 1737 s, 1728 s, 1650 w, 1447 w, 1351 w, 1158 w, 1071 w, 765 w; MS, m/z (relative intensity, %) 232 (24), 215 (10), 214 (62), 202 (18), 201 (11), 187 (25), 186 (41), 185 (13), 174 (16), 173 (12), 172 (11), 170 (11), 169 (45), 158 (11), 157 (26), 156 (11), 155 (47), 154 (11), 153 (12), 145 (21), 144 (24), 143 (58), 142 (56), 141 (35), 131 (14), 130 (25), 129 (100), 128 (70), 127 (26), 117 (44), 116 (24), 115 (93), 105 (22), 103 (17), 102 (12), 91 (54), 89 (12), 77 (28), 65 (13), 63 (11); exact mass calcd for 232.1100, found 232.1100.



major-**28**



minor-**28**

Butenolide 30 (Table 2, entry 13). GC analysis of the crude reaction mixture showed that a mixture of major-**30** and minor-**30** were produced in a ratio of 99/1. (major-**30**); White solid; mp 100-104 °C (hexane/AcOEt = 2/1); R_f 0.16 (hexane/AcOEt = 1/1); ^{1}H NMR ($CDCl_3$) δ 2.43 (bs, 4H), 3.53 (s, 2H), 3.68 (t, J = 4.2 Hz, 4H), 4.94 (s, 2H), 7.37-7.46 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 54.0, 55.3, 66.7, 71.3, 125.0, 128.5, 128.8, 129.0, 141.9, 158.7; IR (KBr): 2860 w, 1831 w, 1754 s, 1737 s, 1665 w, 1493 w, 1443 m, 1352 w, 1295 w, 1208 w, 1114 m, 1038 w, 1010 m, 863 w, 789 w, 740 w, 700 w; MS, m/z (relative intensity, %) 260 (15), 259 (90), 258 (14), 215 (13), 214 (77), 184 (15), 174 (30), 173 (17), 172 (81), 156 (11), 145 (10), 144 (24), 143 (12), 130 (19), 129 (40), 128 (20), 117 (40), 116 (38), 115 (99), 100 (16), 89 (11), 86 (100), 56 (31); exact mass calcd for 259.1208, found 259.1214.

Butenolide 32 (Table 2, entry 14). GC analysis of the crude reaction mixture showed that a mixture of major-**32** and minor-**32** were produced in a ratio of 57/43. Both isomers can be separated by preparative HPLC. (major-**32**); White solid; mp 141-143 °C (hexane/CH_2Cl_2 = 2/1) R_f 0.15 (hexane/AcOEt = 2/1); ^{1}H NMR ($CDCl_3$) δ 1.99-2.06 (m, 2H), 2.59 (t, J = 7.9 Hz, 2H), 3.75 (t, J = 6.7 Hz, 2H), 5.03 (s, 2H), 7.34-7.41 (m, 5H), 7.69-7.74 (m, 2H), 7.81-7.85 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.9, 26.5, 37.7, 70.7, 123.2, 126.4, 127.1, 129.2, 130.2, 131.1, 132.0, 133.9, 156.1, 168.3, 174.6; IR (KBr): 3855 w, 3745 w, 3630 w, 2952 w, 1752 s, 1709 s, 1654 w, 1618 w, 1496 w, 1438 m, 1400 s, 1367 m, 1208 m, 1101 w, 1058 s, 1006 s, 901 w, 774 m, 723 m, 700 m, 614 w, 530 w, 410 w; MS, m/z (relative intensity, %):
(minor-**32**); White solid; mp 158-162 °C (hexane/CH_2Cl_2 = 1/1); R_f 0.15 (hexane/AcOEt = 2/1); ^{1}H NMR ($CDCl_3$) δ 1.94 (tt, J = 7.3 Hz, J = 8.0 Hz, 2H), 2.68 (t, J = 8.0 Hz, 2H), 3.71 (t, J = 7.3 Hz, 2H), 4.87 (s, 2H), 7.32-7.41 (m, 5H), 7.71-7.76 (m, 2H), 7.82-7.86 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 25.1, 26.6, 37.4, 70.9, 123.3, 127.4, 128.6, 128.8, 129.6, 131.8, 134.1, 160.1, 168.2, 173.1; IR (KBr): 3855 w, 3745 w, 3630 w, 2943 w, 1744 s, 1709 s, 1654 w, 1560 w, 1497 w, 1468 w, 1433 m, 1403 m, 1371 m, 1350 m, 1259 w, 1191 w, 1130 m, 1106 m, 1021 m, 961 w, 885 w, 795 w, 721 m, 703 m, 647 w, 530 w, 485 w; MS, m/z (relative intensity, %) 347 (35), 281 (12), 207 (28), 188 (15), 187 (100), 174 (31), 161 (17), 160 (39), 143 (14), 141 (12), 133 (11), 130 (11), 129 (13), 128 (18), 117 (17), 115 (24), 104 (11), 77 (17), 76 (10); exact mass calcd for 347.1158, found 347.1163.

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