Supporting Information for

Bismuth-Catalyzed Intramolecular Carbo-oxycarbonylation of 3-Alkynyl Esters

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General Methods. Nuclear magnetic resonance spectra were taken on JEOL EX-270 (^{1}H NMR, 270.05 MHz; 67.8 MHz; ^{13}C NMR) spectrometer or JEOL Lambda-400 (^{1}H NMR, 395.75 MHz; 99.5 MHz; ^{13}C NMR) spectrometer using residual chloroform (for ^{1}H NMR, 7.26 ppm) and $CDCl_3$ (for ^{13}C NMR, 77.0 ppm) as an internal standard. LRMS (EI) was obtained at 70 eV on a Shimazu QP-5050 spectrometer. HRMS experiments were performed by analytical center at Hiroshima University. Microanalyses were performed at our analytical laboratory. Melting points were uncorrected and were recorded on YANAKO micro melting point apparatus. Column chromatography was performed with silica gel Merck 60 (Merck, type 60, 230-400 mesh). TLC monitoring was performed with silica gel aluminium sheets (Merck, type 60 F_{254}). 1,4-Dioxane, hexane, tetrahydrofuran, and toluene were distilled from Na/benzophenone ketyl. Acetonitrile and nitromethane were distilled from P_2O_5 and stored over molecular sieves. Dichloroethane were distilled from CaH_2. $Bi(OTf)_3$ was purchased from Aldrich (Cat. No. 633305) and used as received. Molecular sieve 4Å (beads; >2 mm) was purchased from Merck (Lot. No. 1.05708.0250) and dried with heat-gun for 1 h prior to use. Unless otherwise noted, commercially available reagents were used without further purification.

Preparation of starting materials

2,2-dimethyl methyl pentynoate [CAS No. 86101-49-7].

Freshly prepared lithium diisopropy lamide (251.9 mmol) in THF (200 mL) was added a solution of methyl isobutyrate (23.4 g, 229 mmol) in THF (25 mL) through a dropping funnel over 2 h with stirring at 0 °C. After complete addition, the reaction mixture stirred for 1 h at room temperature before cooling back to 0 °C. A solution of propargyl bromide (18.0 mL, 242 mmol) in THF (25 mL) was then added dropwisely. The mixture was warmed to room temperature and then stirred for 19 h. After quenching with water, the organic layer was separated and the aqueous layer extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated. The obtained oily material was distilled (48-51 °C, 14-15 mmHg) to give 13.4 g of the product (42%) as colorless oil.

2,2-dimethyl-5-phenyl methyl pentynoate [CAS No. 182809-45-6].

2,2-dimethyl methyl pentynoate (2.5 g, 17.8 mmol) was added to a solution of triethylamine (18 mL)

and iodobenzene (3.6 g, 17.8 mmol). $Pd(PPh_3)_2Cl_2$ (75 mg, 0.1 mmol), CuI (54 mg, 0.3 mmol), and PPh_3 (103 mg, 0.4 mmol) were added. The reaction mixture was refluxed for 10 h. After quenching with water, the organic layer was separated and the aqueous layer extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated. The obtained oily material was purified by column chromatography (25% chloroform in hexanes) to afford the product as a yellow oil (70 %).

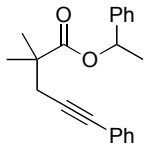
2,2-Dimethyl-5-phenyl-4-pentynoic acid [CAS No. 334474-15-6].

To a solution of NaOH (2.50 g, 62.4 mmol) in methanol (10 mL) was added a solution of 2,2-dimethyl-5-phenyl methyl pentynoate (2.7 g, 12.5 mmol) in methanol (15 mL). The mixture was heated at 80 °C for 16 h. After cooling to room temperature, the crude mixture was concentrated and then diluted with H_2O (15 mL). The aqueous mixture was extracted with Et_2O. The aqueous layer was acidified with concentrated HCl and extracted with Et_2O. The combined extracts were washed with brine, dried over $MgSO_4$, filtrated, and concentrated. The obtained solid was purified by column chromatography (33% ethyl acetate in hexane) to give the acid (1.34 g, 53%).

General method for preparation of the alkynyl esters 1.

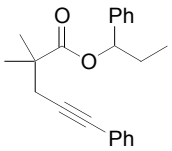
After addition of the carboxylic acid (2.47 mmol), PPh_3 (2.7 mmol), the alcohol (2.47 mmol), and dry THF (25 mL) in 10-mL round bottom flask, the flask was cooled to 0 ºC. The mixture was slowly added DEAD (430 mg, 2.47 mmol), and then stirred at 0 ºC. After 1h, the solution was warmed to room temperature, and additionally stirred for 14 h. The mixture was added saturated Na_2SO_4 solution. The aqueous layer was extracted with ether, and the combined ethereal solution was dried over Na_2SO_4, filtered, concentrated. The ester **1** was obtained by purification of the crude product with a silica-gel column chromatography.

2,2-Dimethyl-5-phenylpent-4-ynoic acid-1-phenylethyl ester (1a).



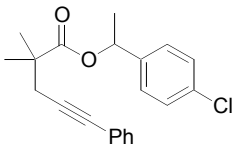
Isolated in 70% yield as a colorless oil; R_f (Hexane / EtOAc = 30, SiO_2) = 0.22; ^1H NMR ($CDCl_3$, 395.75 MHz) δ 1.33 (6H, s, CCH_3), 1.52 (3H, d, J = 6.5 Hz, $CHCH_3$), 2.66 (2H, s, CCH_2), 5.87 (1H, q, J = 6.5 Hz, OCH), 7.22-7.36 (10H, m, Ph); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 22.3, 24.59, 24.65, 30.5, 42.5, 72.4, 82.7, 86.7, 123.6, 125.8, 126.3, 127.7, 128.1, 128.4, 131.6, 141.8, 175.8; LRMS m/z 306 (M^+, 3.7), 291 (11), 115 (24), 105 ($PhCHCH_3$, 100), 77 (18). Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.42; H, 7.26.

2,2-Dimethyl-5-phenylpent-4-ynoic acid 1-phenylpropyl ester (1b).



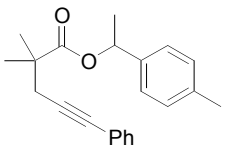
Isolated in 90% yield as a colorless oil; R_f (Hexane / EtOAc = 30, SiO_2) = 0.26; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ .91 (3H, d, *J* = 7.2 Hz, CH_2CH_3), 1.35 (6H, d, *J* = 1.6 Hz, CCH_3), 1.74-2.02 (2H, m, $CHCH_2$), 2.69 (2H, s, CCH_2), 5.68 (1H, dd, *J* = 7.6, 5.9 Hz, OCH), 7.21-7.34 (10H, m, Ph); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 9.9, 24.66, 24.70, 29.6, 30.5, 42.6, 77.2, 82.8, 86.7, 123.6, 126.2, 127.6, 127.7, 128.1, 128.3, 131.6, 140.7, 175.9; LRMS m/z 320 (M^+, 0.59), 291 (16), 118 (45), 91 ($PhCH_2$, 100). Anal. Calcd for $C_{22}H_{24}O_2$: C, 82.46; H, 7.55. Found: C, 82.55; H, 7.25.

2,2-Dimethyl-5-phenylpent-4-ynoic acid-1-(4-chlorophenyl)ethyl ester (1c).



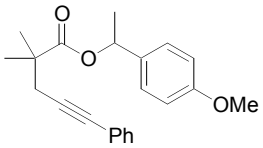
Isolated in 39% yield as a colorless oil; R_f (Hexane / EtOAc = 30, SiO_2) = 0.17; ^{1}H NMR ($CDCl_3$, 395.75 MHz) δ 1.33 (6H, d, *J* = 2.7 Hz, CH_3, 1.51 (3H, d, *J* = 6.5 Hz, $CHCH_3$), 2.66 (2H, s, CCH_2), 5.84 (1H, q, *J* = 6.5 Hz, OCH), 7.23-7.31 (9H, m, Ph); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 22.2, 24.7, 30.6, 42.6, 71.8, 82.8, 86.5, 123.5, 127.3, 127.8, 128.2, 128.6, 131.5, 133.5, 140.3, 175.8; LRMS m/z 340 (M^+, 2.8), 325 (10), 141 (44), 139 (4-$ClPhCHCH_3$, 100), 115 (34), 103 (54). HRMS Calcd for [$C_{21}H_{21}ClO_2$]: 340.1230. Found: 340.1226.

2,2-Dimethyl-5-phenylpent-4-ynoic acid 1-(4-tolyl)ethyl ester (1d).



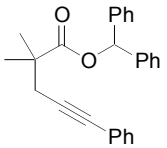
Isolated in 84% yield as a colorless oil; R_f (Hexane / EtOAc = 10, SiO_2) = 0.5; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 1.32 (6H, s, CCH_3), 1.51 (3H, d, *J* = 9.7 Hz, $CHCH_3$), 2.30 (3H, s, $PhCH_3$), 2.66 (2H, s, CCH_2), 5.85 (1H, q, *J* = 9.7 Hz, OCH), 7.09-7.33 (9H, m, Ph); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 21.1, 22.2, 24.57, 24.61, 30.5, 42.5, 72.4, 82.7, 86.7, 123.6, 125.8, 127.6, 128.1, 129.1, 131.5, 137.4, 138.8, 175.8; LRMS m/z 320 (M^+, 2.4), 305 (11), 119 (4-$MePhCHCH_3$, 100). HRMS Calcd for [$C_{22}H_{24}O_2$]: 320.1776. Found: 320.1779.

2,2-Dimethyl-5-phenylpent-4-ynoic acid-1-(4-methoxyphenyl)ethyl ester (1e).



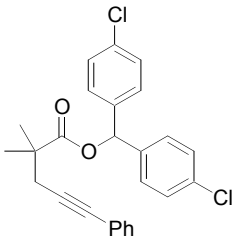
Isolated in 74% yield as a colorless oil; R_f (Hexane / EtOAc = 10, SiO_2) = 0.43; ^1H NMR ($CDCl_3$, 395.75 MHz) δ 1.32 (6H, d, *J* = 2.4 Hz, CCH_3), 1.52 (3H, d, *J* = 6.5 Hz, $CHCH_3$), 2.66 (2H, s, CCH_2), 3.77 (3H, s, OCH_3), 5.86 (1H, q, *J* = 6.5 Hz, OCH), 6.82 (2H, d, *J* = 8.7 Hz, Ph), 7.25-7.32 (7H, m, Ph); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 22.1, 24.60, 24.63, 42.5, 55.2, 72.2, 82.7, 86.7, 113.8, 123.6, 127.3, 127.7, 128.1, 131.6, 133.9, 159.1, 175.9; LRMS m/z 336 (M^+, 0.8), 321 (5), 135 (4-MeOPhCHCH$_3$, 100). HRMS Calcd for [$C_{22}H_{24}O_3$]: 336.1725. Found: 336.1728.

2,2-Dimethyl-5-phenylpent-4-ynoic acid diphenylmethyl ester (1f).



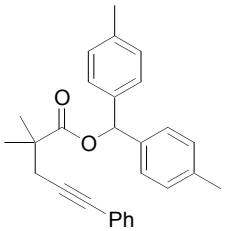
Isolated in 66% yield as a white solid (mp. 83-84 ºC); R_f (Hexane / EtOAc = 10, SiO_2) = 0.38; ^1H NMR ($CDCl_3$, 270.05 MHz) δ 1.38 (6H, s, CCH_3), 2.73 (2H, s, $CHCH_2$), 6.87 (1H, s, OCH), 7.23-7.36 (15H, m, Ph); ^{13}C NMR ($CDCl_3$, 67.80 MHz) (one peak was not observed) δ 24.7, 30.5, 42.7, 77.1, 82.9, 86.6, 123.5, 127.0, 127.7, 127.8, 128.1, 128.3, 128.5, 130.1, 131.6, 132.4, 140.3, 175.6; LRMS m/z 368 (M^+, 1.3), 167 (PhCHPh, 100), 165 (27), 152 (12), 115 (11). Anal. Calcd for $C_{26}H_{24}O_2$: C, 84.75; H, 6.57. Found: C, 84.54; H, 6.55.

2,2-Dimethyl-5-phenylpent-4-ynoic acid di(4-chlorophenyl)methyl ester (1g).



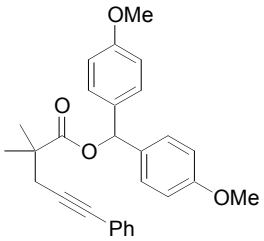
Isolated in 67% yield as a white solid (mp. 87-88 ºC); R_f (Hexane / EtOAc = 30, SiO_2) = 0.24; ^1H NMR ($CDCl_3$, 270.05 MHz) δ 1.37 (6H, s, CCH_3), 2.70 (2H, s, CCH_2), 6.79 (1H, s, OCH), 7.25-7.26 (13H, m, Ph); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 24.7, 30.6, 42.8, 75.7, 83.0, 86.3, 123.3, 127.8, 128.2, 128.3, 128.8, 131.5, 133.9, 138.3, 175.3; LRMS data was not obtained. Anal. Calcd for $C_{26}H_{22}Cl_2O_2$: C, 71.40; H, 5.07. Found: C, 71.35; H, 4.95.

2,2-Dimethyl-5-phenylpent-4-ynoic acid di(4-tolyl)methyl ester (1h).



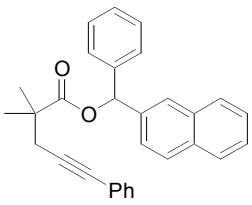
Isolated in 55% yield as a white solid (mp. 83-84 ºC); R_f (Hexane / EtOAc = 10, SiO_2) = 0.43; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 1.37 (6H, s, CCH_3), 2.30 (6H, s, $PhCH_3$), 2.71 (2H, s, CCH_2), 6.80 (1H, s, OCH), 7.08 (4H, d, *J* = 7.9 Hz, Ph), 7.21-7.27 (9H, m, Ph); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 21.1, 24.7, 30.5, 42.7, 82.9, 86.6, 123.6, 126.9, 127.6, 128.1, 129.1, 131.6, 137.4, 137.5, 175.6; LRMS m/z 396 (M^+, 1.06), 195 [$(4\text{-MePh})_2CH^+$], 100), 180 (14), 165 (17). Anal. Calcd for $C_{28}H_{28}O_2$: C, 84.81; H, 7.12. Found: C, 84.51; H, 6.86.

2,2-Dimethyl-5-phenylpent-4-ynoic acid di(4-methoxyphenyl)methyl ester (1i).



Isolated in 22% yield as a white solid (mp. 92-93 ºC); R_f (Hexane / EtOAc = 10, SiO_2) = 0.43; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 1.36 (6H, s, CCH_3), 2.70 (2H, s, CCH_2), 3.75 (6H, s, OCH_3), 6.79-6.82 (5H, m, OCH, Ph), 7.23-7.26 (9H, m, Ph); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 24.7, 30.6, 42.7, 55.2, 77.0, 82.9, 86.7, 113.8, 123.6, 127.7, 128.1, 128.3, 131.6, 132.7, 159.1, 175.6; LRMS data was not obtained. Anal. Calcd for $C_{28}H_{28}O_4$: C, 78.48; H, 6.59. Found: C, 78.32; H, 6.44.

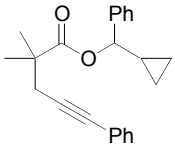
2,2-Dimethyl-5-phenylpent-4-ynoic acid naphthalen-2-yl-phenylmethyl ester (1j).



Isolated as a white solid (mp. 100-101 ºC); R_f (Hexane / EtOAc = 10, SiO_2) = 0.35; ^{1}H NMR ($CDCl_3$, 395.75 MHz) δ 1.40 (6H, d, *J* = 1.7 Hz, CCH_3), 2.75 (2H, s, CCH_2), 7.04 (1H, s, OCH_2), 7.17-7.48 (13H, m, Ph), 7.74-7.83 (4H, m, Ph); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 24.71, 24.75, 30.6, 42.8, 77.2, 82.9, 86.5, 123.5, 124.9, 126.17, 126.20, 127.0, 127.6, 127.7, 127.8, 128.06, 128.14, 128.4, 128.5, 131.6, 132.9,

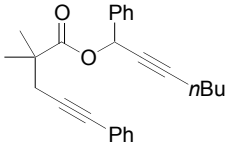
133.0, 137.6, 140.1, 175.6; LRMS data was not obtained. Anal. Calcd for $C_{36}H_{26}O_2$: C, 86.09; H, 6.26. Found: C, 85.87; H, 6.50.

2,2-Dimethyl-5-phenylpent-4-ynoic acid cyclopropylphenylmethyl ester (1k).



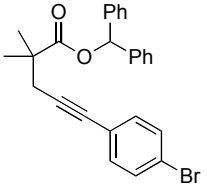
Isolated in 84% yield as a colorless oil; R_f (Hexane / Chloroform = 2, SiO_2) = 0.16; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 0.39-0.88 (4H, m, $CHCH_2CH_2$), 1.23-1.36 (1H, m, OCHCH), 1.36 (6H, s, CCH_3), 2.70 (2H, s, $CCCH_2$), 5.29 (1H, d, *J* = 8.6 Hz, OCH_2), 7.23-7.41 (13H, m, Ph), 7.23-7.41 (10H, m, Ph); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 3.0, 3.6, 16.6, 24.6, 24.7, 30.5, 42.7, 79.4, 82.7, 86.7, 123.6, 126.4, 127.65, 127.68, 128.1, 128.3, 131.6, 140.5, 175.9; LRMS m/z 332 (M^+, 0.39), 304 (8), 228 (10), 131 ($PhCHCHCH_2CH_2$, 100), 115 (18), 91 (30). Anal. Calcd for $C_{23}H_{24}O_2$: C, 83.10; H, 7.28. Found: C, 82.95; H, 7.32.

2,2-Dimethyl-5-phenylpent-4-ynoic acid 1-phenylhept-2-ynyl ester (1l).



Isolated in 82% yield as a yellow oil; R_f (Hexane / EtOAc = 30, SiO_2) = 0.22; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 0.89 (3H, t, *J* = 7.2 Hz, CH_2CH_3), 1.35 (6H, d, *J* = 1.3 Hz, CH_3), 1.38-1.52 (4H, m, CH_2CH_2), 2.22 (2H, td, *J* = 6.9, 2.0 Hz, CCH_2CH_2), 2.67 (2H, d, *J* = 1.3 Hz, CCH_2), 6.48 (1H, t, *J* = 2.0 Hz, OCH), 7.25-7.60 (10H, m, Ph); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 13.5, 18.4, 21.8, 24.4, 24.5, 30.36, 30.41, 42.5, 66.2, 76.6, 82.8, 86.5, 88.2, 123.6, 127.3, 127.6, 128.1, 128.38, 128.42, 131.6, 137.7, 175.5; LRMS m/z 372 (M^+, 3.5), 329 (22), 171 (63), 142 (46), 129 (86), 115 (90), 91 ($PhCH_2$, 100). Anal. Calcd for $C_{26}H_{28}O_2$: C, 83.83; H, 7.58. Found: C, 82.98; H, 7.76.

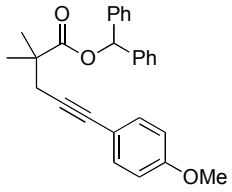
2,2-Dimethyl-5-(4-bromophenyl)pent-4-ynoic acid benzhydryl ester (1m).



Isolated in 56% yield as a white solid (mp. 91-92 ºC); R_f (Hexane / EtOAc = 10, SiO_2) = 0.43; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 1.37 (6H, s, CCH_3), 2.70 (2H, s, CCH_2), 6.87 (1H, s, OCH), 7.10 (2H, d, *J*

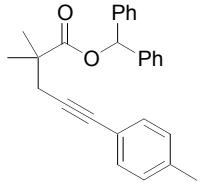
= 8.6 Hz, Ph), 7.25-7.39 (12H, m, Ph); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 24.7, 30.5, 42.7, 77.1, 81.9, 87.9, 121.8, 122.4, 126.9, 127.8, 128.5, 131.3, 133.0, 140.2, 175.4; LRMS m/z 448 (M^{+1}, 1.1), 167 ($CHPh_2$, 100), 152 (11), 141 (7). Anal. Calcd for $C_{26}H_{23}BrO_2$: C, 69.80; H, 5.18. Found: C, 69.91; H, 5.11.

2,2-Dimethyl-5-(4-methoxyphenyl)pent-4-ynoic acid diphenylmethyl ester (1n).



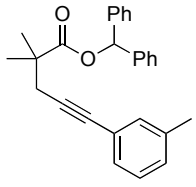
Isolated in 46% yield as a white solid (mp. 59-60 ºC); R_f (Hexane / EtOAc = 10, SiO_2) = 0.29; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 1.37 (6H, s, CCH_3), 2.71 (2H, s, CCH_2), 3.80 (3H, s, OCH_3), 6.76-6.81 (2H, m, Ph), 6.86 (1H, s, OCH), 7.21-7.37 (12H, m, Ph); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 24.7, 30.6, 42.8, 55.3, 77.1, 82.7, 84.9, 113.7, 115.7, 127.0, 127.8, 128.5, 133.0, 140.3, 159.1, 175.6; LRMS data was not obtained. Anal. Calcd for $C_{27}H_{26}O_3$: C, 81.38; H, 6.58. Found: C, 81.40; H, 6.48.

2,2-Dimethyl-5-(4-tolyl)pent-4-ynoic acid diphenylmethyl ester (1o).



Isolated in 48% yield as a white solid (mp. 97-98 ºC); R_f (Hexane / EtOAc = 10, SiO_2) = 0.44; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 1.38 (6H, s, CCH_3), 2.33 (3H, s, $PhCH_3$), 2.72 (2H, s, CCH_2), 6.86 (1H, s, OCH), 7.06 (2H, d, *J* = 7.9 Hz, Ph), 7.19 (2H, d, *J* = 7.9 Hz, Ph), 7.27-7.34 (10H, m, Ph); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 21.4, 24.7, 30.5, 42.7, 77.1, 83.0, 85.7, 120.5, 127.0, 127.8, 128.5, 128.9, 131.5, 137.7, 140.3, 175.6; GC- LRMS data was not obtained. Anal. Calcd for $C_{27}H_{26}O_2$: C, 84.78; H, 6.85. Found: C, 84.51; H, 6.71.

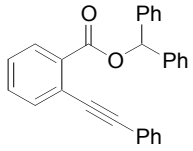
2,2-Dimethyl-5-(3-tolyl)pent-4-ynoic acid diphenylmethyl ester (1p).



Isolated in 48% yield as a white solid (mp. 40-41 ºC); R_f (Hexane / EtOAc = 10, SiO_2) = 0.39; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 1.38 (6H, s, CCH_3), 2.30 (3H, s, $PhCH_3$), 2.72 (2H, s, CCH_2), 6.87 (1H, s, OCH), 7.11-7.38 (14H, m, Ph); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 21.2, 24.7, 30.5, 42.7, 77.1, 83.0, 86.1, 123.3, 127.0, 127.8, 128.0, 128.4, 128.59, 128.63, 132.2, 137.7, 140.2, 175.6; LRMS data was not

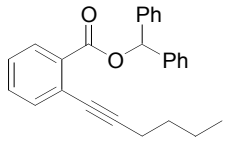
obtained. Anal. Calcd for $C_{27}H_{26}O_2$: C, 84.78; H, 6.85. Found: C, 84.73; H, 6.74.

1-Phenylethynylbenzoic acid benzhydryl ester (1q).



Isolated in 97% yield as a yellow solid (mp. 82-83 °C); R_f (Hexane / EtOAc = 10, SiO_2) = 0.36; ^{1}H NMR ($CDCl_3$, 395.75 MHz) δ 7.19-7.53 (18H, m, Ph, OCH), 7.67 (1H, d, *J* = 7.0 Hz, Ph), 8.09 (1H, d, *J* = 7.0 Hz, Ph); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 78.0, 88.4, 94.6, 123.2, 123.9, 127.3, 127.8, 127.9, 128.2, 128.4, 128.5, 130.8, 131.6, 131.7, 131.8, 134.4, 140.2, 165.3; LRMS data was not obtained. Anal. Calcd for $C_{28}H_{20}O_2$: C, 86.57; H, 5.19. Found: C, 86.23; H, 5.40.

2-Hex-1-ynyl-benzoic acid benzhydryl ester (1r).

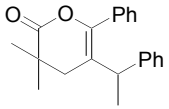


Isolated in 77% yield as a yellow oil; R_f (Hexane / EtOAc = 10, SiO_2) = 0.53; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 0.90 (3H, t, *J* = 7.2 Hz, CH_2CH_3), 1.34-1.56 (4H, m, CH_2CH_2), 2.32 (2H, t, *J* = 6.9 Hz, CCH_2), 7.15 (1H, s, OC*H*), 7.25-7.54 (13H, m, Ph), 7.98 (1H, dd, *J* = 7.9, 1.3 Hz, Ph); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 13.6, 19.5, 22.1, 30.6, 77.7, 96.4, 124.7, 127.1, 127.2, 127.8, 128.4, 130.4, 131.58, 131.65, 134.5, 140.3, 165.5; LRMS data was not obtained. Anal. Calcd for $C_{26}H_{24}O_2$: C, 84.75; H, 6.57. Found: C, 85.01; H, 6.67s.

General procedure of the carbo-oxycarbonylation of alkynyl esters 1 with $Bi(OTf)_3$.

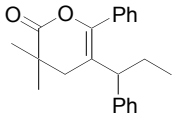
In a 20 mL Schlenk tube, molecular sieves (100 mg) was dried with heat-gun under vacuum for 2 h and purged argon, and then cooled to room temperature. The alkynyl ester 1 (0.16 mmol) and 1,2-dichloroethane (1.6 mL) was added (267 mg, 1 mmol), and stirred for 1 h at room temperature. After addition of $Bi(OTf)_3$ (0.016 mmol) to the mixture, stirring was continued under appropriate conditions with monitoring silica-gel TLC. If NMR yield was measured, appropriate amount of internal standard (mesitylene) was added at this time. The obtained mixture was passed through a silica-gel short column with ether as an eluent, concentrated. The product was afforded by means of column chromatography.

3,3-Dimethyl-6-phenyl-5-(1-phenylethyl)-3,4-dihydropyran-2-one (2a).



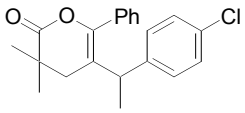
Isolated as a white solid (mp. 114-115 ºC); R_f (Hexane / EtOAc = 30, SiO_2) = 0.13; ^{1}H NMR ($CDCl_3$, 395.75 MHz) δ 1.07 (3H, s, CCH_3), 1.25 (3H, s, CCH_3), 1.45 (3H, d, *J* = 6.9 Hz, $CHCH_3$), 1.89 (1H, d, *J* = 16.8 Hz, CCHH), 2.15 (1H, d, *J* = 16.8 Hz, CHCH), 4.02 (1H, q, *J* = 6.9 Hz, CCH), 7.13-7.49 (10H, m, Ph); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 17.1, 24.48, 24.57, 34.1, 35.9, 38.0, 117.7, 126.5, 127.2, 128.3, 128.4, 128.7, 128.9, 133.1, 142.6, 145.6, 174.0; LRMS m/z 306 (M^+, 25.5), 263 (19), 145 (18), 105 ($PhCHCH_3$, 100), 77 (72), 70 (55). Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.42; H, 7.22.

3,3-Dimethyl-6-phenyl-5-(1-phenylpropyl)-3,4-dihydropyran-2-one (2b).



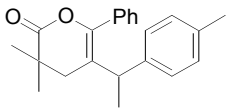
Isolated as a white solid (mp. 97-98 ºC); R_f (Hexane / EtOAc = 30, SiO_2) = 0.26; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 0.95 (3H, t, *J* = 7.4 Hz, CH_2CH_3), 0.99 (3H, s, CCH_3), 1.29 (3H, s, CCH_3), 1.72-2.02 (2H, m, $CHCH_2$), 1.94 (1H, d, *J* = 16.7 Hz, CCHH), 2.26 (1H, d, *J* = 16.7 Hz, CCHH), 3.72 (1H, t, *J* = 7.8 Hz, CCH), 7.03-7.51 (10H, m, Ph); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 12.3, 23.8, 24.2, 24.9, 34.1, 35.9, 45.8, 116.5, 126.5, 127.6, 128.3, 128.4, 128.9, 129.2, 133.3, 142.1, 146.3, 173.9; LRMS m/z 320 (M^+, 11.7), 291 (48), 263 (61), 105 (PhCO, 100), 91 (22), 77 (42). Anal. Calcd for $C_{22}H_{24}O_2$: C, 82.46; H, 7.55. Found: C, 82.77; H, 7.53.

5-[1-(4-Chlorophenyl)-ethyl]-3,3-dimethyl-6-phenyl-3,4-dihydropyran-2-one (2c).



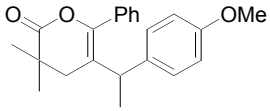
Isolated as a white solid (mp. 93-94 ºC); R_f (Hexane / EtOAc = 10, SiO_2) = 0.23; ^{1}H NMR ($CDCl_3$, 395.75 MHz) δ 1.11 (3H, s, CCH_3), 1.29 (3H, s, CCH_3), 1.45 (3H, d, *J* = 7.2 Hz, $CHCH_3$), 1.88 (1H, d, *J* = 16.8 Hz, CCHH), 2.16 (1H, d, *J* = 16.8 Hz, CCHH), 4.03 (1H, q, *J* = 7.2 Hz, CCH), 7.08-7.49 (9H, m, Ph); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 17.1, 24.53, 24.56, 34.1, 35.9, 37.6, 117.1, 128.4, 128.5, 128.6, 128.7, 129.1, 132.3, 132.9, 141.1, 145.9, 173.7; LRMS m/z 340 (M^+, 17.7), 297 (15), 105 (PhCO, 100), 77 (71), 70 (99). Anal. Calcd for $C_{21}H_{21}ClO_2$: C, 74.00; H, 6.21. Found: C, 74.06; H, 6.26.

3,3-Dimethyl-6-phenyl-5-(1-p-tolylethyl)-3,4-dihydropyran-2-one (2d).



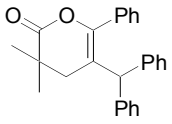
The completely pure material was not obtained. The ^{1}H and/or ^{13}C NMR data given were selected from spectra recorded of samples. Isolated as a colorless oil; R_f (Hexane / EtOAc = 10, SiO_2) = 0.34; ^{1}H NMR ($CDCl_3$, 395.75 MHz) δ 1.11 (3H, s, CCH_3), 1.28 (3H, s, CCH_3), 1.44 (3H, d, *J* = 6.9 Hz, $CHCH_3$), 1.93 (1H, d, *J* = 16.8 Hz, CCHH), 2.16 (1H, d, *J* = 16.8 Hz, CCHH), 2.32 (3H, s, $PhCH_3$), 4.00 (1H, q, *J* = 6.9 Hz, CCH), 6.93-7.12 (4H, m, Ph), 7.35-7.52 (5H, m, Ph); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 17.2, 20.9, 25.5, 34.1, 35.9, 37.6, 117.8, 127.1, 128.4, 128.7, 128.9, 129.0, 129.1, 133.1, 136.0, 139.5, 145.5, 174.0; LRMS m/z 320 (M^+, 30.4), 305 (16), 277 (24), 235 (36), 159 (38), 105 (PhCO, 100), 77 (51). HRMS Calcd for [$C_{22}H_{24}O_2$]: 320.1776. Found: 320.1781.

5-[1-(4-Methoxyphenyl)-ethyl]-3,3-dimethyl-6-phenyl-3,4-dihydropyran-2-one (2e).



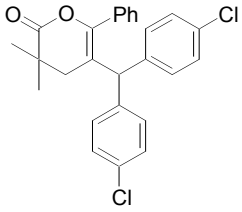
The completely pure material was not obtained. The ^{1}H and/or ^{13}C NMR data given were selected from spectra recorded of samples. Isolated as a colorless oil; R_f (Hexane / EtOAc = 10, SiO_2) = 0.15; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 1.10 (3H, s, CCH_3), 1.28 (3H, s, CCH_3), 1.44 (3H, d, *J* = 6.9 Hz, $CHCH_3$), 1.91 (1H, d, *J* = 16.8 Hz, CCHH), 2.16 (1H, d, *J* = 16.8 Hz, CCHH), 3.79 (3H, s, OCH_3), 4.00 (1H, q, *J* = 6.9 Hz, CCH), 6.79-7.09 (4H, m, Ph), 7.39-7.52 (5H, m, Ph); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 17.3, 24.52, 24.55, 34.1, 35.9, 37.2, 55.2, 113.6, 118.0, 128.1, 128.4, 128.7, 128.9, 131.6, 133.1, 145.3, 158.1, 174.0; LRMS m/z 336 (M^+, 25.2), 321 (24), 293 (22), 251 (20), 175 (20), 135 (28), 105 (PhCO, 100), 77 (56). HR LRMS Calcd for [$C_{22}H_{24}O_3$]: 336.1725. Found: 336.1721.

5-Benzhydryl-3,3-dimethyl-6-phenyl-3,4-dihydropyran-2-one (2f).



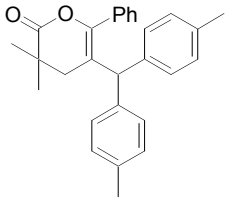
Isolated as a white solid (mp. 161-162 ºC); R_f (Hexane / EtOAc = 10, SiO_2) = 0.22; ^{1}H NMR ($CDCl_3$, 395.75 MHz) δ 1.16 (6H, s, CCH_3 x 2), 2.27 (2H, s, CCH_2), 5.30 (1H, s, CCH), 7.07-7.43 (15H, m, Ph); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 24.6, 35.8, 36.2, 51.5, 114.4, 126.8, 128.0, 128.41, 128.43, 128.48, 129.0, 129.2, 132.9, 141.7, 147.7, 173.8; LRMS m/z 368 (M^+, 13.7), 283 (27), 207 (28), 167 (28), 165 (26), 105 (PhCO, 100), 77 (55). Anal. Calcd for $C_{26}H_{24}O_2$: C, 84.75; H, 6.57. Found: C, 84.85; H, 6.70.

5-[Bis-(4-chlorophenyl)-methyl]-3,3-dimethyl-6-phenyl-3,4-dihydropyran-2-one (2g).



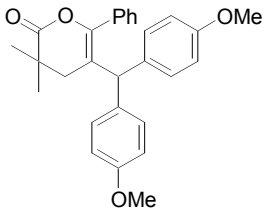
Isolated as a white solid (mp. 144-145 ºC); R_f (Hexane / EtOAc = 5, SiO_2) = 0.41; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 1.18 (6H, s, CCH_3 x 2), 2.20 (2H, s, CCH_2), 5.21 (1H, s, CCH), 7.03 (4H, d, *J* = 8.2 Hz, Ph), 7.26-7.37 (9H, m, Ph); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 24.6, 35.7, 36.2, 50.4, 113.2, 128.3, 128.5, 128.7, 129.4, 130.2, 132.5, 132.8, 139.8, 148.3, 173.2; LRMS data was not obtained. Anal. Calcd for $C_{26}H_{22}Cl_2O_2$: C, 71.40; H, 5.07. Found: C, 71.70; H, 5.18.

5-Di-p-tolylmethyl-3,3-dimethyl-6-phenyl-3,4-dihydropyran-2-one (2h).



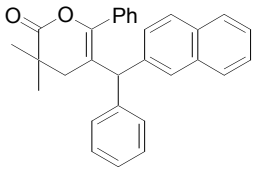
Isolated as a white solid (mp. 153-154 ºC); R_f (Hexane / EtOAc = 5, SiO_2) = 0.52; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 1.16 (6H, s, CCH_3 x 2), 2.25 (2H, s, CCH_2), 2.34 (6H, s, 4-CH_3Ph x 2), 5.21 (1H, s, CCH), 7.00 (4H, d, *J* = 8.1 Hz, Ph), 7.12 (4H, d, *J* = 8.1 Hz, Ph), 7.24-7.44 (5H, m, Ph); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 21.0, 24.6, 35.8, 36.2, 50.7, 114.8, 128.3, 128.5, 128.9, 129.1, 132.9, 136.2, 138.8, 147.3, 173.8; LRMS m/z 396 (M^+, 12.9), 311 (32), 297 (23), 105 (PhCO, 100), 77 (49); Anal. Calcd for $C_{28}H_{28}O_2$: C, 84.81; H, 7.12. Found: C, 85.07; H, 7.25.

5-[Bis-(4-methoxyphenyl)-methyl]-3,3-dimethyl-6-phenyl-3,4-dihydropyran-2-one (2i).



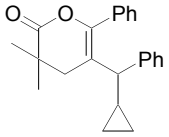
Isolated as a white solid (mp. 165-166 ºC); R_f (Hexane / EtOAc = 5, SiO_2) = 0.30; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 1.17 (6H, s, CCH_3 x 2), 2.24 (2H, s, CCH_2), 3.81 (6H, s, OCH_3 x 2), 5.18 (1H, s, CCH), 6.83-7.04 (8H, m, Ph), 7.35-7.43 (5H, m, Ph); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 24.7, 35.8, 36.3, 49.9, 55.3, 113.8, 115.0, 128.4, 128.5, 129.1, 130.0, 132.9, 134.1, 147.2, 158.3, 173.9; LRMS data was not obtained. Anal. Calcd for $C_{28}H_{28}O_4$: C, 78.48; H, 6.59. Found: C, 78.36; H, 6.63.

3,3-Dimethyl-5-(naphthalen-2-yl-phenylmethyl)-6-phenyl-3,4-dihydropyran-2-one (2j).



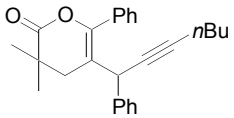
Isolated as a white solid; (mp. 162-163 ºC); R_f (Hexane / EtOAc = 10, SiO_2) = 0.37; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 1.15 (3H, s, CCH_3), 1.21 (3H, s, CCH_3), 2.26 (1H, d, *J* = 17.1 Hz, CCHH), 2.37 (1H, d, *J* = 17.1 Hz, CCHH), 5.45 (1H, s, CCH), 7.12-7.86 (17H, m, Ph);
^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 24.6, 24.8, 36.0, 36.3, 51.7, 114.3, 125.9, 126.2, 126.9, 127.3, 127.5, 127.6, 127.8, 128.1, 128.4, 128.5, 129.2, 132.3, 132.8, 133.3, 139.3, 141.8, 147.8, 173.7; LRMS data was not obtained. Anal. Calcd for $C_{30}H_{26}O_2$: C, 85.92; H, 6.28. Found: C, 86.09; H, 6.26.

5-(Cyclopropylphenylmethyl)-3,3-dimethyl-6-phenyl-3,4-dihydropyran-2-one (2k).



The completely pure material was not obtained. The ^{1}H and/or ^{13}C NMR data given were selected from spectra recorded of samples. Isolated as a colorless oil; R_f (Hexane / EtOAc = 10, SiO_2) = 0.31; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 0.02-0.20 (2H, m, $CHCH_2$), 0.49-0.59 (1H, m, CHCHH), 0.71-0.81 (1H, m, CHCHH), 1.12-1.23 (1H, m, CHCH), 1.19 (3H, s, CCH_3), 1.35 (3H, s, CCH_3), 2.14 (1H, d, *J* = 16.8 Hz, CCHH), 2.33 (1H, d, *J* = 16.8 Hz, CCHH), 2.97 (1H, d, *J* = 10.2 Hz, CCH), 7.25-7.45 (10H, m, Ph); ^{13}C NMR ($CDCl_3$, 68.7 MHz) δ.; 4.1, 6.6, 13.4, 24.7, 24.8, 35.2, 36.2, 49.4, 116.5, 126.6, 127.7, 128.4, 128.9, 133.0, 142.1, 146.5, 174.0; LRMS m/z 332 (M^+, 2.90), 215 (38), 131 (35), 105 (PhCO, 100), 91 (26), 77 (54). HRMS Calcd for [$C_{23}H_{24}O_2$]: 332.1776. Found: 332.1768.

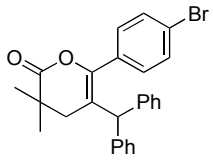
3,3-Dimethyl-6-phenyl-5-(1-phenylhept-2-ynyl)-3,4-dihydropyran-2-one (2l).



Isolated as a yellow oil; R_f (Hexane / EtOAc = 30, SiO_2) = 0.40; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 0.96 (3H, t, *J* = 7.1 Hz, CH_2CH_3), 1.15 (3H, s, CCH_3), 1.31 (3H, s, CCH_3), 1.42-1.65 (4H, m, CH_2CH_2), 1.95 (1H, d, *J* = 17.0 Hz, CCHH), 2.26 (1H, d, *J* = 17.0 Hz, CCHH), 2.35 (2H, td, *J* = 6.9, 2.3 Hz, CCH_2CH_2), 4.89 (1H, t, *J* = 2.3 Hz, OCH), 7.21-7.63 (10H, m, Ph); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 13.6, 18.5, 22.0, 24.3, 24.7, 31.1, 35.0, 36.0, 38.3, 77.9, 85.7, 114.5, 127.0, 127.5, 128.3, 128.5, 128.7, 129.2, 132.5, 138.4, 146.2, 173.9; LRMS m/z 372 (M^+, 6.08), 287 (13), 231 (19), 105 (PhCO, 100), 77 (56).

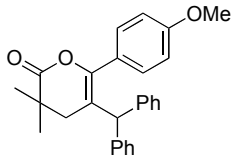
HRMS Calcd for [$C_{26}H_{28}O_2$]: 372.2089. Found: 372.2091.

3,3-Dimethyl-5-diphenylmethyl-6-(4-bromophenyl)-3,4-dihydropyran-2-one (2m).



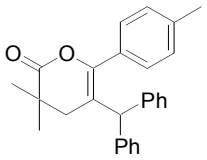
Isolated as a white solid; (mp. 206-207 ºC); R_f (Hexane / EtOAc = 10, SiO_2) = 0.40; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 1.15 (6H, s, CCH_3), 2.25 (2H, s, CCH_2), 5.23 (1H, s, CCH), 7.09-7.12 (4H, m, Ph), 7.26-7.36 (8H, m, Ph), 7.47-7.52 (2H, m, Ph); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 24.6, 35.9, 36.2, 51.6, 115.2, 123.4, 126.9, 128.5, 129.0, 130.1, 131.6, 131.7, 141.5, 146.6, 173.5; LRMS date was not obtained. Anal. Calcd for $C_{26}H_{23}BrO_2$: C, 69.80; H, 5.18. Found: C, 69.54; H, 5.05.

3,3-Dimethyl-5-diphenylmethyl-6-(4-methoxyphenyl)-3,4-dihydropyran-2-one (2n).



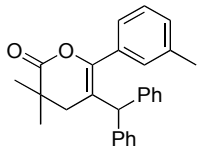
Isolated as a white solid; (mp. 185-186 ºC); R_f (Hexane / EtOAc = 10, SiO_2) = 0.21; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 1.15 (6H, s, CCH_3), 2.23 (2H, s, CCH_2), 3.81 (3H, s, OCH_3), 5.30 (1H, s, CCH), 6.87 (2H, d, *J* = 8.2 Hz, Ph), 7.12 (4H, d, *J* = 7.3 Hz, Ph), 7.25-7.36 (8H, m, Ph); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 24.6, 35.8, 36.3, 51.6, 55.2, 113.6, 113.7, 125.3, 126.7, 128.4, 129.0, 129.8, 141.9, 147.5, 160.1, 173.9; LRMS date was not obtained. Anal. Calcd for $C_{27}H_{26}O_3$: C, 81.38; H, 6.58. Found: C, 81.33; H, 6.69.

5-Benzhydryl-3,3-dimethyl-6-(4-tolyl)-3,4-dihydropyran-2-one (2o).



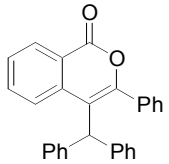
Isolated as a white solid (mp. 166-167 ºC); R_f (Hexane / Chloroform = 1, SiO_2) = 0.38; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 1.14 (6H, s, CCH_3), 2.24 (2H, s, CCH_2), 2.36 (3H, s, $PhCH_3$), 5.30 (1H, s, CCH), 7.10-7.35 (14H, m, Ph); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 21.3, 24.6, 35.8, 36.2, 51.5, 114.0, 126.7, 128.3, 128.4, 129.0, 130.0, 139.1, 141.8, 147.8, 173.8; LRMS m/z 382 (M^+, 17.6), 297 (37), 167 (26), 119 (4-MePhCO, 100), 91 (55). Anal. Calcd for $C_{27}H_{26}O_2$: C, 84.78; H, 6.85. Found: C, 84.30; H, 6.85.

3,3-Dimethyl-5-diphenylmethyl-6-(3-methylphenyl)-3,4-dihydropyran-2-one (2p).



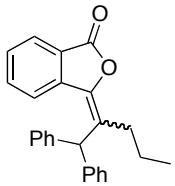
Isolated as a white solid; (mp. 63-64 ºC); R_f (Hexane / EtOAc = 10, SiO_2) = 0.32; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 1.16 (6H, s, CCH_3), 2.25 (2H, s, CCH_2), 2.33 (3H, s, $PhCH_3$), 5.30 (1H, s, CCH), 7.11-7.36 (14H, m, Ph); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 21.4, 24.6, 35.8, 36.2, 51.5, 114.3, 125.6, 126.7, 128.2, 128.4, 129.0, 129.1, 129.9, 132.7, 138.1, 141.8, 147.8, 173.9; LRMS m/z 382 (M^+, 26.5), 297 (39), 207 (24), 167 (29), 119 (4-MePhCO, 100), 91 (75). Anal. Calcd for $C_{27}H_{26}O_2$: C, 84.78; H, 6.85. Found: C, 84.88; H, 6.74.

4-Benzhydryl-3-phenyl-isochromen-1-one (2q).



Isolated as a white solid (mp. 199-200 ºC); R_f (Hexane / EtOAc = 10, SiO_2) = 0.26; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 5.86 (1H, s, CC*H*), 7.18-7.45 (18H, m, Ph), 8.33-8.39 (1H, m, Ph); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 49.7, 106.3, 115.2, 121.8, 126.7, 127.3, 127.7, 128.4, 128.5, 129.0, 129.1, 129.8, 129.9, 133.3, 133.6, 137.3, 141.2, 154.2; LRMS data was not obtained. HRMS Calcd for [$C_{28}H_{20}O_2$]: 388.1463. Found: 388.1460.

3-(1,1-Diphenylpentan-2-ylidene)isobenzofuran-1(3H)-one (2r').



Isolated as *E*/*Z* mixture (colorless oil); R_f (Hexane / EtOAc = 10, SiO_2) = 0.28; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ *E*-isomer: 0.63 (3H, t, *J* = 7.2 Hz, CH_2CH_3), 0.94-1.20 (4H, m, $CH_3CH_2CH_2$), 2.39-2.45 (2H, m, CCH_2), 5.89 (1H, s, CC*H*), 7.20-7.98 (14 H, m, Ph), *Z*-isomer: 0.71 (3H, t, *J* = 7.2 Hz, CH_2CH_3), 0.94-1.20 (4H, m, $CH_3CH_2CH_2$), 2.51-2.58 (2H, m, CCH_2), 6.05 (1H, s, CC*H*), 7.20-7.98 (14 H, m, Ph); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ *E*-isomer: 13.4, 23.05, 30.7, 31.3, 51.5, 123.7, 126.7, 127.0, 128.3, 128.5, 128.9, 129.42, 129.44, 134.5, 137.9, 1413, 143.0, *Z*-isomer: 13.5, 23.07, 29.2, 30.8, 51.8, 122.9, 125.8, 126.8, 127.1, 128.1, 128.6, 128.7, 129.0, 129.7, 134.1, 138.2, 141.5, 143.8; LRMS data was not obtained. Anal. Calcd for $C_{25}H_{22}O_2$: C, 84.72; H, 6.26. Found: C, 84.33; H, 6.15.