Supporting Information

A Tyrosine-derived Bonzofuranone Related to Diazonamide A

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***N*-(2,2,2-Trichloroethoxycarbonyl)-*L*-tyrosine methyl ester**

$NaHCO_3$ (7.3 g, 86.3 mmol) and 50 mL 10% $NaHCO_3$ aqueous solution and 50 mL ether was placed in a 500 mL three neck round bottom flask fitted with magnetic stir-bar and a dropping funnel, and the apparatus was cooled to 0EC in an ice-water bath. *L*-Tyrosine methyl ester hydrochloride (20.0 g, 86.3 mmol; Aldrich) was added gradually over 10 min. Trichloroethyl chloroformate (18.3 g, 86.3 mmol; Aldrich) in 30 mL ether was then added through the dropping funnel over 2.5 h. The reaction mixture was stirred at room temperature for 10 h, and 15 mL 10% $NaHCO_3$ was added. The reaction mixture was then stirred for 2 h, diluted with ca 100 mL ether and the layers were separated. The aqueous layer was extracted by ether (3 x 40 mL). The combined organic layer was washed by water (50 mL), brine (50 mL), and dried (Na_2SO_4). After filtration and evaporation (aspirator), the residue was filtered through a short silica column (5 x 9 cm) eluted with ether. Solvent removal (aspirator) yielded 31.0 g of the title compound in 97% yield; analytical tlc on silica gel, 2:1 hexane/EtOAc, Rf= 0.44; Molecular ion calcd for $C_{13}H_{14}Cl_3N_1O_5$: 1136.7490; found m/e= 368.9952, error= 4 ppm; IR (CH_2Cl_2, cm^{-1}) 3594, N-H; 1735, C=O; 300 MHz NMR (8.5:1.5 mixture of two rotamers; $CDCl_3$, ppm) ä 6.96 (2H, d, J= 8.4 Hz) 6.72 (2H, d, J= 8.4 Hz) 6.60 (1H, s) 5.75 (0.85H, d, J= 8.1 Hz) 5.55 (0.15H, d, J= 8.1 Hz) 4.76 (1H, AB, J= 12.3 Hz) 4.73-4.60 (1H, m) 4.72-4.60 (1H, m) 4.65 (1H, AB, J= 12.3 Hz) 3.73 (3H, s) 3.09 (1H, ABX, J= 14.1, 3.0 Hz) 3.00 (1H, ABX, J= 14.1, 6.0 Hz).

1-(3-Bromo-2-methoxyphenyl)ethanol (5)

The procedure of Nishiyama was used with modification.[5] ^{i}PrMgCl (30.2 mL, 2.0 M in ether, Aldrich) was placed in 250 mL oven-dried round bottom flask fitted with magnetic stir-bar under N_2. The ether solvent was evaporated with a nitrogen stream, 10 mL anhydrous THF was added and evaporated again with nitrogen stream. The residue was then dissolved in 50 mL anhydrous THF over 10 min. To the resulting solution was added dibromoanisole **$3** (4.01 g, 15.9 mmol). The reaction mixture was stirred at 40-45 EC (oil bath temperature) for 8 h and cooled to room temperature. Acetaldehyde (6.7 mL, 11.9 mmol; Aldrich) was added in one portion via a cold syringe. The mixture was stirred for 20 min at room temperature, and was quenched with 30 mL sat NH_4Cl(aq). The organic layer was separated, and the aqueous layer was extracted with ether (3 x 20 mL). The combined organic layers were washed with brine and dried (Na_2SO_4). After solvent removal the residue was purified by flash chromatography on silica gel (5 x 17 cm) using EtOAc/hexane (1:5) to afford the desired product **5** 3.0 g (84%) in fractions 49-83 (10 mL/fraction); analytical tlc on silica gel, 3:1 hexane/EtOAc, Rf= 0.41; M-15 calcd for $C_8H_8O_2Br_1$: 214.9708; found m/e= 214.9724, error= 7ppm; IR (CH_2Cl_2, cm^{-1}) 3359, O-H; 300 MHz NMR ($CDCl_3$, ppm) ä 7.45 (1H, dd, J= 8.0, 1.5 Hz) 7.39 (1H, dd, J= 8.0, 1.5 Hz) 7.00 (1H, dd, J= 8.0, 8.0 Hz) 5.17 (1H, dd, J= 6.3, 3.9 Hz) 3.86 (3H, s) 2.69 (1H, d, J= 3.9 Hz) 1.47 (3H, d, J= 6.3 Hz).

3-Bromo-2-methoxyacetophenone

A solution of 15.5 mL CH_2Cl_2 and 0.66 mL DMSO was cooled to -78 EC. Oxaloyl chloride (0.41 mL) was added dropwise and the mixture was stirred 20 min. The alcohol **5** (0.536 g, 2.32 mmol) was then added by cannula as a solution in 4 mL CH_2Cl_2 and stirring was maintained 30 min.

Triethylamine (3.23 mL, 10 equiv) was then added in one portion. After 5 min, the mixture was warmed to 0 EC, stirred 30 min, and warmed to rt and stirred 30 min. Ether (150 mL) was added, and the mixture was washed with satd sodium bicarbonate (75 mL), dried ($MgSO_4$) and evaporated (aspirator) to an oil. The residue was purified by flash chromatography on silica gel (4 x 18 cm) using EtOAc/Hex (1:10) to provide 0.50 g (94%) of the ketone product; analytical tlc on silica gel, 8:1 hexane/EtOAc, Rf= 0.39. Molecular ion calcd for $C_9H_9Br_1O_2$: 227.97858; found m/e= 227.9790; error= 2ppm; IR (CH_2Cl_2, cm^{-1}) 1684, C=O; 300 MHz NMR ($CDCl_3$, ppm) ä 7.70 (1H, dd, J= 8.1, 1.8 Hz) 7.57 (1H, dd, J= 8.1, 1.8 Hz) 7.07 (1H, dd, J= 8.1, 8.1 Hz) 3.88 (3H, s) 2.65 (3H, s).

á-Chloro-3-bromo-2-methoxyacetophenone (6)

The procedure of Kajigaeshi was used with modification.[10] Thus, 3-bromo-2-methoxyacetophenone from above (5.51 g, 24.1 mmol) was placed in a 500 mL flask fitted with a condenser and magnetic stir-bar, and 145 mL 1,2-dichloroethane and 56 mL of a 6:1 solution of AcOH:water were added, followed by $BnMe_3NCl_2I$[10] (18.8 g, 54.1 mmol). The mixture was then warmed to 65 EC (oil bath temperature) and stirred for 4.5 h. After cooling to room temperature, the organics were diluted with ether and washed with 5% $NaHSO_3$ until the organic layer was clear, followed by washing with 5% $NaHCO_3$ to remove acetic acid. After drying over $MgSO_4$, solvent was evaporated to provide 6.13 g (96%) of solid chloroketone **6**, sufficiently pure for use in the next step. A sample was crystallized from ether, mp 54.5-55.5 EC; analytical tlc on silica gel, 1:1 hexane/EtOAc, Rf= 0.68. Molecular ion calcd for $C_9H_8Br_1Cl_1O_2$: 263.93770; found m/e= 263.9371, error= 2 ppm; IR (CH_2Cl_2, cm^{-1}) 1698, C=O; 300 MHz NMR ($CDCl_3$, ppm) ä 7.76 (1H, dd, J= 9.6, 2.4 Hz) 7.63 (1H, dd, J= 9.6, 2.4 Hz) 7.12 (1H, dd, J= 9.6, 9.6 Hz) 4.75 (2H, s) 3.92 (3H, s).

2(*S*)-(2,2,2-Trichloroethoxycarbonylamino)-3-{4-[2-(3-bromo-2-methoxyphenyl)-2-oxo-ethyl]-phenyl}-propionic acid methyl ester (8)

To a solution of the *N*-protected *L*-tyrosine methyl ester **7** (dried over molecular sieves, 6.07 g, 16.4 mmol) in 40 mL anhydrous CH_2Cl_2 was added K_2CO_3 (flame dried under vacuum, 2.27 g, 16.4 mmol) and the ketone **6** (dried over molecular sieves, 2.02 g, 7.54 mmol). The reaction mixture was stirred at room temperature for 72 h, poured into 220 mL 0.3 N HCl at 0 EC and extracted with ether (3 x 100 mL). The combined organic layers were washed with brine, and dried (Na_2SO_4). After filtration and concentration (aspirator) the residue was purified by flash chromatography on silica gel (5 x 15 cm) using CH_2Cl_2/Et_2O (25:1) to provide 3.20 g (71% based on **6**) of ketone **8** as an oil in fractions 14-31 (20 mL/fraction); analytical tlc on silica gel, 2:1 hexane/EtOAc, Rf= 0.35; Molecular ion found for $C_{22}H_{21}N_1O_7Cl_3Br_1$: 596.9547, found m/e= 596.9538, error= 2ppm; IR (CH_2Cl_2, cm^{-1}) 1733, C=O; 300 MHz NMR ($CDCl_3$, ppm) ä 7.76 (1H, dd, J= 7.8, 1.8 Hz) 7.66 (1H, dd, J= 7.8, 1.8 Hz) 7.12 (1H, dd, J= 7.8, 7.8 Hz) 7.04 (2H, d, J= 9.0 Hz) 6.84 (2H, d, J= 9.0 Hz) 5.48 (1H, d, J= 8.1 Hz) 5.20 (2H, s) 4.77 (1H, d, J= 11.7 Hz) 4.66 (1H, ddd, J= 6.0, 6.0, 8.1 Hz) 4.67 (1H, d, J= 11.7 Hz) 3.96 (3H, s) 3.74 (3H, s) 3.12 (1H, dd, J= 13.8, 6.0 Hz) 3.06 (1H, dd, J= 13.8, 6.0 Hz).

2(*S*)-(2,2,2-Trichloroethoxycarbonylamino)-3-[3-(3-bromo-2-methoxyphenyl)-benzofuran-5-yl]-propionic acid methyl ester (9)

The procedure of Baziard-Mouysset was used with modification.[11] Thus, ketone **8** (2.46 g, 4.11 mmol)) was placed in an oven-dried 500 mL three neck round bottom flask fitted with a condenser and mechanic stirrer and 50 mL anhydrous benzene was added. After mechanical stirring for 5 min, polyphosphoric acid (300 g, Aldrich) was gradually added over 15 min. The reaction

mixture was warmed and stirred for 5 h at 90 EC (oil bath temperature). The light brown reaction mixture was cooled to room temperature and gradually poured into 800 mL ice-water. The aqueous solution was then extracted with ether (4 x 80 mL). The combined organic layers were washed with ca 50 mL water, 50 mL 10% $NaHCO_3$, brine, and dried (Na_2SO_4). After filtration and solvent removal (aspirator) the residue was purified by flash chromatography on silica gel (5 x 15 cm) using EtOAc/hexane (1:4) to afford 2.01 g (84%) desired product **9** in fractions 42-55 (10 mL/fraction); analytical tlc on silica gel, 3:1 hexane/EtOAc, Rf= 0.55; M + H^+ calcd for $C_{22}H_{20}N_1O_6Cl_3Br_1$: 577.9540, HRFAB found m/e= 577.9540, error= 0 ppm; IR (CH_2Cl_2, cm^{-1}) 3351, N-H; 1739, C=O; 300 MHz NMR ($CDCl_3$, ppm) ä 7.93 (1H, s) 7.57 (1H, dd, J= 8.1, 1.8 Hz) 7.51-7.46 (3H, m) 7.12-7.08 (2H, m) 5.54 (1H, d, J= 7.8 Hz) 4.77 (1H, d, J= 12.0 Hz) 4.74-4.69 (1H, m) 4.65 (1H, d, J= 12.0 Hz) 3.80 (3H, s) 3.55 (3H, s) 3.31 (1H, dd, J= 14.1, 5.1 Hz) 3.24 (1H, dd, J= 14.1, 4.8 Hz).

2(*S*)-(2,2,2-Trichloroethoxycarbonylamino)-3-[3-(3-bromo-2-methoxyphenyl)-2-oxo-2,3-dihydrobenzofuran-5-yl]-propionic acid methyl ester (10)

Peracetic acid (2.77 mL, 32%, 14.2 mmol, Aldrich) was gradually added to a solution of benzofuran **9** (0.277 g, 0.478 mmol) in 27.7 mL CH_2Cl_2. The mixture was stirred for 48 h and diluted with CH_2Cl_2 to a volume of 75 mL. The organic layer was washed with H_2O (30 mL), 10% $NaHSO_3$ (30 mL), 5% $NaHCO_3$ (30 mL), brine, and dried ($MgSO_4$). After filtration and evaporation (aspirator) the residue was purified by flash chromatography on silica gel (2 x 17 cm) using EtOAc/hexane (1:3) to give 0.231 g lactone **10** (81%) in fractions 9-15 (10 mL/fraction); analytical tlc on silica gel, 3:1 hexane/EtOAc, Rf= 0.18; M + Na^+ calcd for $C_{22}H_{19}N_1O_7Cl_3Br_1Na_1$: 615.9306, HRFAB(+NaI) found m/e= 615.9312, error= 1 ppm; IR (CH_2Cl_2, cm^{-1}) 3345, N-H; 1816, C=O;

1733, C=O; 300 MHz NMR (1:1 mixture of two diastereomers; $CDCl_3$, ppm) ä 7.54 (1H, dd, J= 7.8, 1.8 Hz) 7.15-7.05 (3H, m) 7.00 (1H, ddd, J= 8.1, 8.1, 1.2 Hz) 6.84-6.80 (1H, m) 5.57 (0.5H, d, J= 7.8 Hz) 5.53 (0.5H, d, J= 8.1 Hz) 4.97 (1H, s) 4.80-4.50 (3H, m) 3.67 (1.5H, s) 3.62 (3H, s) 3.55 (1.5H, s) 3.16-2.96 (2H, m).

Enol Carbonate 12

The procedure of Black was used with modification.[7] To a stirred, cooled (0 EC) solution of lactone **10** (0.30 g, 0.50 mmol) in 15 mL anhydrous THF was added NaH (0.023 g, 0.59 mmol; 60% dispersion in mineral oil, Aldrich) in one portion under N_2. The reaction mixture was stirred for 1.5 h at 0 EC before the granular NaH completely disappeared (the solution became light yellow). Chloroformate **11** (previously made as described below for the preparation of **15**; 0.158 M THF solution, 4.6 mL, 7.3 mmol) was added slowly at 0 EC. The reaction mixture was then warmed to room temperature and stirred for 12 h (the light yellow color disappeared and a white precipitate was observed). After solvent evaporation (aspirator) the residue was diluted with 30 mL ether, acidified with 20 mL 0.01 N HCl and extracted with ether (3 x 15 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated (aspirator) to give a viscous oil. It was purified by flash chromatography using CH_2Cl_2/hexane/EtOAc (5:5:1) to afford 0.37 g (92%) of enol carbonate **12** in fractions 18-26 (5 mL/fraction); analytical tlc on silica gel, 5:5:1 CH_2Cl_2/hexane/EtOAc, Rf= 0.56; M + Na^+ calcd for $C_{35}H_{33}N_1O_9Cl_3Br_1Na_1$: 818.0302, HRFAB(+NaI) found m/e= 818.0305, error= 0 ppm; IR (CH_2Cl_2, cm^{-1}) 3450, N-H; 1779, C=O; 300 MHz NMR (9:1 mixture of rotamers; $CDCl_3$, ppm) ä 7.56 (1H, dd, J= 7.8, 1.5 Hz) 7.32 (1H, d, J= 8.4 Hz) 7.28-7.14 (6H, m) 7.11 (1H, dd, J= 7.2, 1.2 Hz) 7.03 (1H, dd, J= 8.7, 2.1 Hz) 6.94 (1H, dd, J= 8.1, 8.1 Hz) 5.48 (0.9H, d, J= 8.1

Hz) 5.20 (0.1H, d, J= 8.1 Hz) 4.88 (1H, ddd, J= 10.5, 10.5, 3.9 Hz) 4.76 (1H, AB, J= 12.0 Hz) 4.70-4.66 (1H, m) 4.67 (1H, AB, J= 12.0 Hz) 3.77 (3H, s) 3.39 (3H, s) 3.26 (1H, ABX, J= 14.1, 4.8 Hz) 3.18 (1H, ABX, J= 14.1, 4.8 Hz) 2.73 (1H, ddd, J= 12.0, 12.0, 3.6 Hz) 2.30-2.18 (1H, m) 2.00-1.85 (2H, m) 1.77 (1H, d, J= 12.0 Hz) 1.68-1.25 (4H, m).

Benzofuranone 13

The carboxylation procedure of Black was used with modification.[7] To a stirred solution of enol carbonate **12** (0.010 g, 0.012 mmol) in 1 mL anhydrous THF was added DMAP (0.0015 g, 0.012 mmol, Aldrich) in 0.1 mL anhydrous THF. The reaction mixture became purple blue immediately, and the blue color slowly disappeared over 12 h. The reaction mixture was then diluted with 8 mL ether, washed with 2 mL 0.1 N HCl, brine and dried (Na_2SO_4). After filtration and evaporation the residue was purified by flash chromatography (1 x 10 cm) using hexane/EtOAc (4:1) to provide 0.0094 g (94%) **13** as a mixture of two diastereomers (3.3:1) in fractions 10-14. The diastereomer ratio was determined by ^{1}H NMR. The diastereomers were separated by preparative HPLC on a silica column (Si 83-101-C, DYNAMAX-60A) using hexane/*i*-PrOH (99.5:0.5) with 1 mL/min; R_T: 9.8 min (minor diastereomer); analytical tlc on silica gel, 3:1 hexane/EtOAc, Rf= 0.31; M + Na^+ calcd for $C_{35}H_{33}N_1O_9Cl_3Br_1Na_1$: 818.0302, HRFAB(+NaI) found m/e= 818.0305, error= 0 ppm; IR (CH_2Cl_2, cm^{-1}), 1819, C=O, 1735, C=O; 300 MHz NMR ($CDCl_3$, ppm) ä 7.49 (1H, dd, J= 7.8, 1.5 Hz) 7.13-6.98 (6H, m) 6.89-6.80 (2H, m) 6.72 (1H, d, J= 2.7 Hz) 6.69 (1H, dd, J= 7.8, 1.5 Hz) 5.38 (1H, d, J= 8.1 Hz) 5.05-4.90 (1H, m) 4.71 (2H, ABq, J= 11.7 Hz) 4.59-4.55 (1H, m) 3.76 (3H, s) 3.70 (3H, s) 3.12-3.00 (2H, m) 2.67 (1H, ddd, J= 11.7, 11.7, 3.6 Hz) 2.35-2.23 (1H, m) 1.95-1.70 (2H, m) 1.60-1.25 (5H, m). ^{13}C NMR (300 MHz, $CDCl_3$, ppm) ä 170.9, 170.8, 165.7,

155.9, 153.5, 152.2, 142.1, 134.9, 131.6, 131.4, 130.9, 128.1, 127.9, 127.4, 127.2, 126.8, 126.3, 126.2, 116.6, 110.7, 95.2, 79.1, 74.7, 61.8, 60.8, 55.0, 52.6, 49.3, 37.7, 33.6, 31.8, 25.5, 24.5; R_T: 11.6 min (major diastereomer); analytical tlc on silica gel, 3:1 hexane/EtOAc, Rf= 0.31; M + Na^+ calcd for $C_{35}H_{33}N_1O_9Cl_3Br_1Na_1$: 818.0302, HRFAB(+NaI) found m/e= 818.0305, error= 0 ppm; IR (CH_2Cl_2, cm^{-1}), 1819, C=O, 1735, C=O; 300 MHz NMR ($CDCl_3$, ppm) ä 7.45 (1H, dd, J= 8.1, 1.5 Hz) 7.25-7.03 (6H, m) 6.69 (1H, dd, J= 7.5, 7.5 Hz) 6.60 (1H, d, J= 1.0 Hz) 6.36 (1H, dd, J= 7.8, 1.5 Hz) 5.44 (1H, d, J= 7.5 Hz) 5.20-5.11 (1H, m) 4.71 (2H, ABq, J= 12.3 Hz) 4.59-4.52 (1H, m) 3.50 (6H, s) 3.05 (1H, ABX, J= 14.1, 5.4 Hz) 2.70 (1H, ddd, J= 11.4, 11.4, 3.3 Hz) 2.70 (1H, ddd, J= 11.4, 11.4, 3.3 Hz) 2.15-2.05 (1H, m) 1.95-1.70 (3H, m) 1.57-1.25 (5H, m). ^{13}C NMR (300 MHz, $CDCl_3$, ppm) ä 171.0, 170.6, 165.6, 155.5, 153.6, 152.5, 142.8, 134.6, 131.7, 131.6, 131.0, 128.5, 127.8, 127.5, 127.3, 126.6, 126.5, 124.7, 116.3, 110.6, 95.3, 79.0, 74.6, 61.5, 61.4, 55.0, 52.3, 49.1, 37.6, 34.5, 31.5, 25.6, 24.6.

Enol Carbonate 15

The following experiment was conducted in a well-vented hood. Thus, to a cooled (-78 EC), stirred solution of phosgene (toxic !,12.28 mL toluene solution 1.93 M, 23.7 mmol; Fluka) in 30 mL anhydrous ether was gradually added a solution of pyridine (freshly distilled, 0.5 mL, 6.2 mmol) and *trans*-1(*S*),2(*R*)-2-phenylcyclohexanol[8] (0.84 g, 4.7 mmol) in 20 mL anhydrous ether over 20 min (white precipitation was observed immediately). The mixture was then warmed to room temperature over 20 min. After solvent evaporation (aspirator in hood) the residue was diluted with 20 mL anhydrous ether and filtered under anhydrous conditions. The filtrate was then concentrated (aspirator with hexane in the trap) to yield a viscous oil with some white solid. After dilution with 5 mL anhydrous

ether, the solution was filtered through a pipette with paper plug under N_2. The resulting solution was dried over molecular sieves for 10 h. The ether solution was then concentrated (N_2 stream) and diluted with 30 mL anhydrous THF to yield the desired chloroformate **11** with the concentration of 0.158 M (assuming 100% yield) in THF, sufficiently pure for the next step.

Then, the carboxylation procedure of Black was used with modification.[7] To a stirred, cooled (0 EC) solution of the 3-phenylbenzofuranone **14**[9] (0.20 g, 0.95 mmol) in 15 mL anhydrous THF was added NaH (0.051 g, 1.29 mmol; 60% dispersion in mineral oil, Aldrich) in one portion under N_2. The reaction mixture was stirred for 1.5 h at 0 EC before NaH completely disappeared (the solution became light yellow). Chloroformate **11** previously prepared (0.158 M THF solution, 6.61 mL, 1.05 mmol) was added slowly at 0EC. The reaction mixture was then warmed to room temperature and stirred for 12 h (the light yellow color disappeared and white precipitate was observed). After solvent evaporation (aspirator) the residue was diluted with 30 mL ether, acidified with 20 mL 0.01 N HCl and extracted with ether (3 x 15 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated (aspirator) to give a viscous oil. The crude product was purified by flash chromatography on silica gel (3 x 17) using EtOAc/hexane (1:8) to afford 0.37 g (93%) of carbonate **15** in fractions 10-17; analytical tlc on silica gel, 8:1 hexane/EtOAc, Rf= 0.33; M + H^+ calcd for $C_{27}H_{25}O_4$: 413.1753, HRFAB found m/e= 413.1753, error= 0 ppm; IR (CH_2Cl_2, cm^{-1}) 1779, C=O; 300 MHz NMR ($CDCl_3$, ppm) ä 7.70-7.64 (1H, m) 7.43-7.15 (13H, m) 4.96-4.84 (1H, m) 2.72 (1H, ddd, J= 12.3, 12.3, 3.3 Hz) 2.30-2.18 (1H, m) 1.98-1.80 (2H, m) 1.79-1.69 (1H, m) 1.65-1.21 (4H, m).

Benzofuranones 16 and 17

The procedure of Black was used with modification.[7] To a stirred solution of enol carbonate **15** (0.050 g, 0.12 mmol) in 3 mL anhydrous CH_2Cl_2 was added DMAP (0.003 g, 0.024 mmol, Aldrich) at 0 EC. The reaction mixture became blue immediately, and the blue color disappeared within 5 min. The reaction mixture was then diluted with 20 mL ether, washed with 5 mL 1 N HCl, brine, and dried (Na_2SO_4). After filtration and evaporation the residue was purified by flash chromatography on silica gel (2 x 17 cm) using EtOAc/hexane (1:6) to provide 0.041 g (82%) as a mixture of two diastereomers (*S*)-**16**/(*R*)-**17** (8.3:1). The diastereomeric ratio was determined by ^{1}H NMR. The major diastereomer (0.037 g) was isolated as a crystalline compound by recrystallization in hexane/ether. Crystals suitable for X-ray crystallography were obtained, mp= 111-113 EC. Removal of solvent provided the minor diastereomer 0.004 g as a viscous oil; (*S*)-**16** (major diastereomer): analytical tlc on silica gel, 6:1 hexane/EtOAc, Rf= 0.48; M + H^+ calcd for $C_{27}H_{25}O_4$: 413.1753, HRFAB found m/e= 413.1753, error= 0 ppm; IR (CH_2Cl_2, cm^{-1}) 1818, C=O; 1731, C=O; 300 MHz NMR (the major diastereomer; $CDCl_3$, ppm) ä 7.35-7.12 (9H, m) 7.09 (1H, dd, J= 8.1, 1.2 Hz) 7.00-6.86 (3H, m) 6.84-6.78 (1H, m) 5.08 (1H, ddd, J= 10.8, 10.8, 4.5 Hz) 2.67 (1H, ddd, J= 12.0, 12.0, 3.6 Hz) 2.14-2.04 (1H, m) 1.97-1.69 (3H, m) 1.60-1.21 (4H, m); ^{13}C NMR (300 MHz, $CDCl_3$, ppm) ä 171.2, 166.9, 153.3, 142.5, 134.8, 130.0, 128.6, 128.5, 128.4, 127.7, 127.4, 126.6, 126.2, 125.1, 124.4, 110.8, 78.9, 62.7, 49.5, 34.1, 31.5, 25.6, 24.5; (*R*)-**17** (minor diastereomer): analytical tlc on silica gel, 6:1 hexane/EtOAc, Rf= 0.48; IR (CH_2Cl_2, cm^{-1}) 1818, C=O; 1731, C=O; 300 MHz NMR ($CDCl_3$, ppm) ä 7.35-7.05 (11H, m) 7.00-6.92 (3H, m) 5.15-5.06 (1H, m) 2.58 (1H, ddd, J= 12.0, 12.0, 3.6 Hz) 2.15-2.05 (1H, m) 2.00-1.70 (3H, m) 1.55-1.20 (4H, m).

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