Supporting Information

Palladium-Catalyzed Synthesis of Novel Optically Active Tryptophan Analogs

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General Information: All reactions were carried out under an atmosphere of dry nitrogen. Solvents were distilled from the appropriate drying agents immediately prior to use. Unless stated otherwise, all chemicals were purchased and used as such. Infrared (IR) spectra were recorded on an ATI Mattson Genesis Series FTIR spectrometer and absorptions are reported in cm^{-1} . NMR spectra were recorded using a Bruker DMX300 (300 MHz) spectrometer from CDCl_3 solutions (unless otherwise reported) using TMS as internal standard. Mass spectra and accurate mass measurements were carried out using a Fisons (VG) Micromass 7070E or a Finnigan MAT900S instrument. R_f values were obtained using thin layer chromatography (TLC) on silica gel-coated plates (Merck silica gel 60 F₂₅₄) with the indicated solvent (mixture). Flash chromatography was performed with Acros Organics silica gel (0.035-0.070 nm). Melting points were determined with a Büchi melting point B-545 apparatus.

General procedure for the Sonogashira cross-coupling reactions: To a solution of the acetylene-containing amino acid, aryl halide (1.2 equiv) and Et_2NH (5 equiv) in Et_2O , CuI (10 mol%) and the Pd -catalyst (5 mol%) were added. The reaction mixture was stirred at room temperature under N_2 -atmosphere. Upon completion (TLC), the reaction mixture was poured into a saturated aqueous solution of NH_4Cl and after separation of the organic layer the aqueous layer was extracted with Et_2O (2x). The combined organic layers were washed with brine, dried (MgSO_4) and concentrated *in vacuo*. The crude product was purified by flash chromatography to afford the pure product.

Methyl 5-(2-aminophenyl)-2-[(*tert*-butoxycarbonyl)amino]-4-pentynoate (5).

Following the general procedure, to a solution of **4** (392 mg, 1.72 mmol), 2-iodoaniline (455 mg, 2.08 mmol) and Et₂NH (0.89 mL, 8.58 mmol) in Et₂O (18 mL), CuI (34 mg, 0.18 mmol) and PdCl₂(PPh₃)₂ (61 mg, 0.09 mmol) were added. Work-up and purification by chromatography (EtOAc/heptane = 1:3) afforded **5** (478 mg, 1.50 mmol, 87%) as a light-brown oil. *R*_f 0.28 (EtOAc/heptane = 1:2); IR (neat) 3369, 2978, 1743, 1711, 1618, 1493; ¹H NMR (300 MHz, CDCl₃) δ 7.17 (dd, *J* = 1.5, 7.6 Hz, 1H, ArH), 7.04 (m, 1H, ArH), 6.59 (m, 2H, ArH), 5.57 (br d, *J* = 8.3 Hz, 1H, NH), 4.56 (m, 1H, NHCHCO₂CH₃), 4.31 (s, 2H, NH₂), 3.73 (s, 3H, CO₂CH₃), 2.95 (d, *J* = 5.2 Hz, 2H, CHCH₂C≡C), 1.42 (s, 9H, C(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃) δ 171.6, 155.1, 148.2, 131.9, 129.3, 117.3, 114.1, 107.3, 88.8, 80.4, 80.0, 52.5, 52.3, 28.1, 24.1; HRMS (EI) calcd for C₁₇H₂₂N₂O₄ 318.1580, found 318.1580.

Methyl 5-[2-(acetylamino)phenyl]-2-[(*tert*-butoxycarbonyl)amino]-4-pentynoate (13**).** Following the general procedure, to a solution of **4** (367 mg, 1.62 mmol), *N*1-(2-iodophenyl)acetamide (465 mg, 1.78 mmol) and Et₂NH (0.74 mL, 8.16 mmol) in Et₂O (18 mL), CuI (32 mg, 0.17 mmol) and PdCl₂(PPh₃)₂ (57 mg, 0.08 mmol) were added. Work-up and purification by chromatography (EtOAc/heptane = 1:2) afforded **13** (471 mg, 1.31 mmol, 81%) as a colorless oil. *R*_f 0.21 (EtOAc/heptane = 1:2); IR (neat) 3329, 2980, 1738, 1693, 1579, 1518, 1444; ¹H NMR (300 MHz, CDCl₃) δ 8.25 (s, 1H, NHCOCH₃), 8.22 (s, 1H, ArH), 7.20 (m, 2H, ArH), 6.88 (m, 1H, ArH), 5.64 (d, *J* = 8.2 Hz, 1H, NH), 4.52 (m, 1H, NHCHCO₂CH₃), 3.68 (s, 3H, CO₂CH₃), 2.93 (dd, *J* = 5.0, 17.2 Hz, 1H, CHCHHC≡C), 2.83 (dd, *J* = 5.9, 17.0 Hz, 1H, CHCHHC≡C), 2.22 (s, 3H, COCH₃), 1.33 (s, 9H, C(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃) δ 171.5, 169.1, 155.2, 139.3, 131.5, 129.0, 123.0, 119.8, 111.8, 90.7, 80.1, 79.0, 52.5, 52.1, 28.0, 24.2, 24.0; HRMS (EI) calcd for C₁₉H₂₄N₂O₅ 360.1685, found 360.1674.

4-[3-(2-aminophenyl)-2-propynyl]-1,3-oxazolan-2-one (14). To a solution of **5** (535 mg, 1.68 mmol) in THF (20 mL), LiBH_4 (73 mg, 3.36 mmol) was added at 0 °C. The reaction mixture was allowed to reach room temperature and stirred for 24 h. Upon completion, the reaction mixture was quenched by adding water (1 mL) and stirred further for 15 min at room temperature, after which time the mixture was poured into water (30 mL). The aqueous layer was extracted with EtOAc (100 mL) and the organic layer was washed with water (30 mL, 2x), brine (30 mL, 2x), dried (MgSO_4), filtrated and concentrated *in vacuo*. The crude product was purified by chromatography (EtOAc/heptane = 1:1) to afford the corresponding amino alcohol (386 mg, 1.33 mmol, 79%) as a light-yellow oil. To a solution of the amino alcohol (366 mg, 1.26 mmol) in THF (30 mL), NaH (52 mg of a 60% dispersion in mineral oil, 1.31 mmol) was added. The reaction mixture was heated at reflux for 22 h, diluted with MeOH (3 mL) and concentrated *in vacuo*. The crude product was purified by chromatography (EtOAc/heptane = 3:1) to afford **14** (179 mg, (0.83 mmol, 66%) as a light-yellow solid. R_f 0.13 (EtOAc/heptane = 2:1); mp 147.2 °C; IR (neat) 3352, 1732, 1614; ^1H NMR (300 MHz, CDCl_3) δ 7.24 (dd, J = 1.7, 8.3 Hz, 1H, ArH), 7.11 (dt, J = 1.6, 7.7 Hz, 1H, ArH), 6.67 (m, 2H, ArH), 5.68 (br s, 1H, NH), 4.57 (dd, J = 8.3, 8.9 Hz, 1H, OCHHCH), 4.28 (dd, J = 4.6, 8.9 Hz, 1H, OCHHCH), 4.18-4.08 (m, 3H, NHCHCH₂ and NH₂), 2.76 (dd, J = 1.4, 5.6 Hz, 2H, CHCH₂C $\equiv$ C); HRMS (EI) calcd for $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_2$ 216.0899, found 216.0898.

Methyl (2S)-6-(2-aminophenyl)-2-[(*tert*-butoxycarbonyl)amino]-5-hexynoate (22**).**

Following the general procedure, to a solution of **21** (518 mg, 2.15 mmol), 2-iodoaniline (565 mg, 2.58 mmol) and Et₂NH (1.12 mL, 10.7 mmol) in Et₂O (20 mL), CuI (40 mg, 0.21 mmol) and PdCl₂(PPh₃)₂ (75 mg, 0.107 mmol) were added. Work-up and purification by chromatography (EtOAc/heptane = 1:3) afforded **22** (562 mg, 1.69 mmol, 79%) as a light-brown oil. *R*_f 0.27 (EtOAc/heptane = 1:2); [α]_D = +4.9 (*c* 1.0, CH₂Cl₂); IR (neat) 3461, 3369, 2975, 1734, 1701, 1617; ¹H NMR (300 MHz, CDCl₃) δ 7.20 (dd, *J* = 1.4, 7.7 Hz, 1H, ArH), 7.03 (m, 1H, ArH), 6.60 (m, 2H, ArH), 5.33 (br d, *J* = 8.5 Hz, 1H, NH), 4.50 (br m, 1H, NHCHCO₂CH₃), 4.32 (br s, 2H, NH₂), 3.69 (s, 3H, CO₂CH₃), 2.53 (t, *J* = 6.9 Hz, 2H, CH₂CH₂C≡C), 2.11 (m, 1H, CHCH₂CH₂), 1.92 (m, 1H, CHCH₂CH₂), 1.42 (s, 9H, C(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃) δ 172.9, 155.4, 148.2, 132.0, 129.0, 117.3, 114.1, 107.9, 93.1, 79.8, 78.3, 52.6, 52.3, 31.5, 28.2, 16.0; HRMS (EI) calcd for C₁₈H₂₄N₂O₄ 332.1736, found 332.1734.

Methyl (2S)-7-(2-aminophenyl)-2-[(*tert*-butoxycarbonyl)amino]-6-heptynoate (25**).** Following the general procedure, to a solution of **24** (322 mg, 1.26 mmol), 2-iodoaniline (337 mg, 1.54 mmol) and Et₂NH (0.67 mL, 6.43 mmol) in Et₂O (18 mL), CuI (27 mg, 0.14 mmol) and PdCl₂(PPh₃)₂ (49 mg, 0.07 mmol) were added.

Work-up and purification by chromatography (EtOAc/heptane = 1:3) afforded **25**

(341 mg, 0.98 mmol, 78%) as a yellow oil. *R*_f 0.26 (EtOAc/heptane = 1:2); [α]_D = +10.8 (*c* 1.0, CH₂Cl₂); IR (neat) 3356, 2978, 1738, 1712, 1614, 1493, 1454; ¹H NMR (300 MHz, CDCl₃) δ 7.22 (dd, *J* = 1.2, 7.5 Hz, 1H, ArH), 7.07 (m, 1H, ArH), 6.65 (m, 2H, ArH), 5.02 (br m, 1H, NH), 4.32 (br m, 1H, NHCHCO₂CH₃), 4.15 (s, 2H, NH₂), 3.75 (s, 3H, CO₂CH₃), 2.52 (t, *J* = 6.9 Hz, 1H, CH₂CHHC≡C), 2.30 (t, *J* = 6.6 Hz, 1H, CH₂CHHC≡C), 2.08-1.56 (m, 4H, CHCH₂CH₂CH₂), 1.46 (s, 9H, C(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃) δ 172.9, 155.2, 147.3, 132.0, 128.9, 117.8, 114.2, 108.6, 94.4, 80.1, 77.9, 53.3, 52.5, 32.2, 28.6, 25.1, 19.6; HRMS (EI) calcd for C₁₉H₂₆N₂O₄ 346.1893, found 346.1900.

Methyl (2S)-5-(2-aminophenyl)-2-[di(*tert*-butoxycarbonyl)amino]-4-pentynoate (15). Following the general procedure, to a solution of the biscarbamate (337 mg, 1.03 mmol), 2-iodoaniline (272 mg, 1.24 mmol) and Et₂NH (0.55 mL, 5.26 mmol) in Et₂O (18 mL), CuI (22 mg, 0.12 mmol) and PdCl₂(PPh₃)₂ (37 mg, 0.05 mmol) were added. Work-up and purification by chromatography (EtOAc/heptane = 1:4) afforded **15** (394 mg, 0.94 mmol, 91%) as a brown oil. *R*_f 0.15 (EtOAc/heptane = 1:4); [α]_D = -89.2 (*c* 0.5, CH₂Cl₂); IR (neat) 3465, 3373, 2980, 1790, 1743, 1695, 1616; ¹H NMR (300 MHz, CDCl₃) δ 7.17 (dd, *J* = 1.2, 7.5 Hz, 1H, ArH), 7.03 (dt, *J* = 1.5, 8.1 Hz, 1H, ArH), 6.59 (m, 2H, ArH), 5.22 (dd, *J* = 6.3, 9.3 Hz, 1H, NCHCO₂CH₃), 4.21 (s, 2H, NH₂), 3.75 (s, 3H, CO₂CH₃), 3.25 (dd, *J* = 6.3, 17.4 Hz, 1H, CHCHHC≡C), 3.18 (dd, *J* = 9.3, 17.4 Hz, 1H, CHCHHC≡C), 1.48 (s, 18H, 2 x C(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃) δ 169.8, 169.4, 151.8, 151.5, 148.0, 132.1, 129.1, 117.4, 114.0, 108.0, 90.6, 83.6, 79.4, 73.5, 67.4, 57.0, 52.6, 28.3, 21.9 HRMS (EI) calcd for C₂₂H₃₀N₂O₆ 418.2104, found 418.2099.

General procedure for the Pd-catalyzed cyclization reactions: To a solution of the cyclization precursor in MeCN, the Pd-catalyst (5 mol%) was added. The reaction mixture was stirred at reflux temperature under N₂-atmosphere. Upon completion (TLC), the reaction mixture was concentrated *in vacuo* and purified by flash chromatography to afford the pure product.

Methyl 5-{2-[(*tert*-butoxycarbonyl)amino]phenyl}-3,4-dihydro-2H-2-pyrrole-carboxylate (6**).** Following the general procedure, to a solution of **5** (340 mg,

1.07 mmol) in MeCN (10 mL), PdCl₂(MeCN)₂ (28 mg, 0.11 mmol) was added.

Purification by chromatography (EtOAc/heptane = 1:6) afforded **6** (222 mg, 0.70 mmol, 65%) as a white solid. *R_f* 0.45 (EtOAc/heptane = 1:2); mp 78.0 °C; IR (neat) 2980, 1734, 1720, 1604, 1576, 1522, 1446; ¹H NMR (300 MHz, CDCl₃) δ 11.9 (s, 1H, *NHCOOC*(CH₃)₃), 8.42 (d, *J* = 8.4 Hz, 1H, ArH), 7.40 (m, 2H, ArH), 6.96 (t, *J* = 8.3 Hz, 1H, ArH), 4.99 (m, 1H, *NCHCO*₂CH₃), 3.78 (s, 3H, CO₂CH₃), 3.25-3.00 (m, 2H, CCH₂CH₂), 2.35-2.09 (m, 2H, CH₂CH₂CH), 1.52 (s, 9H, C(CH₃)₃); ¹³C NMR (100 MHz, CDCl₃) δ 177.4, 172.9, 153.5, 140.9, 131.9, 130.5, 120.8, 118.5, 118.4, 79.7, 74.4, 52.2, 36.9, 28.3, 25.1; HRMS (EI) calcd for C₁₇H₂₂N₂O₄ 318.1580, found 318.1576.

1-(*tert*-butyl) 2-methyl 5-(2-aminophenyl)-2,3-dihydro-1*H*-1,2-pyrrole-dicarboxylate (7). Following the general procedure, to a solution of **5** (424 mg, 1.33 mmol) in MeCN (10 mL), PdCl₂(MeCN)₂ (35 mg, 0.13 mmol) was added.

Purification by chromatography (EtOAc/heptane = 1:3) afforded **7** (227 mg, 0.71 mmol, 54%) as a white solid. *R*_f 0.27 (EtOAc/heptane = 1:3); mp 139.1 °C; IR (neat) 3442, 3357, 2972, 1730, 1668, 1649, 1603, 1402; ¹H NMR (300 MHz, CDCl₃) δ 7.06 (m, 2H, ArH), 6.59 (m, 2H, ArH), 5.00 (dd, *J* = 2.1, 3.5 Hz, 1H, C=CHCH₂), 4.92 (dd, *J* = 2.5, 11.2 Hz, 1H, NCHCO₂CH₃), 4.50 (br s, 2H, NH₂), 3.77 (s, 3H, CO₂CH₃), 3.07 (ddd, *J* = 2.1, 11.2, 18.9 Hz, 1H, C=CHCHHCH), 2.53 (dt, *J* = 3.5, 17.0 Hz, 1H, C=CHCHHCH), 1.14 (s, 9H, C(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃) δ 173.7, 152.1, 145.3, 142.4, 129.2, 129.0, 119.1, 116.6, 114.2, 108.4, 80.5, 60.5, 52.6, 32.0, 27.7; HRMS (EI) calcd for C₁₇H₂₂N₂O₄ 318.1580, found 318.1583.

Methyl 2-[(*tert*-butoxycarbonyl)amino]-5-oxo-5-phenylpentanoate (16**).** Following the general procedure, to a solution of **10** (438 mg, 1.44 mmol) in MeCN (16 mL), PdCl₂(MeCN)₂ (37 mg, 0.14 mmol) was added and the mixture was stirred at room temperature under N₂-atmosphere. Purification by chromatography (EtOAc/heptane = 1:4) afforded **16** (149 mg, 0.46 mmol, 32%) as a light-yellow solid. *R_f* 0.39 (EtOAc/heptane = 1:2); mp 109.4 °C; IR (neat) 3359, 1736, 1699, 1680, 1599, 1514, 1448; ¹H NMR (300 MHz, CDCl₃) δ 7.92 (d, *J* = 7.2 Hz, 2H, ArH), 7.56-7.40 (m, 3H, ArH), 5.14 (br d, *J* = 7.2 Hz, 1H, NH), 4.37 (m, 1H, NHCHCO₂CH₃), 3.73 (s, 3H, CO₂CH₃), 3.18-2.97 (m, 2H, CH₂CH₂CO), 2.36-2.25 (m, 1H, CHCH₂CH₂), 2.16-1.99 (m, 1H, CHCH₂CH₂), 1.41 (s, 9H, C(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃) δ 198.5, 172.7, 155.3, 136.6, 133.1, 128.5, 128.0, 80.1, 53.3, 52.6, 34.8, 28.6, 27.3.

1-(*tert*-butyl) 2-methyl 5-[2-(acetylamino)phenyl]-2,3-dihydro-1*H*-1,2-pyrroledicarboxylate (18**).** Following the general procedure, to a solution of **13** (376 mg, 1.04 mmol) in MeCN (14 mL), PdCl₂(MeCN)₂ (29 mg, 0.11 mmol) was added. Purification by chromatography (EtOAc/heptane = 1:3) afforded **18** (184 mg, 0.51 mmol, 49%) as a white solid. *R*_f 0.25 (EtOAc/heptane = 1:2); mp 108.7 °C; IR (neat) 3357, 2974, 1738, 1684, 1643, 1581, 1524, 1443; ¹H NMR (300 MHz, CDCl₃) δ 8.69 (br s, 1H, NHCOCH₃), 8.44 (d, *J* = 8.3 Hz, 1H, ArH), 7.27 (m, 1H, ArH), 7.16 (dd, *J* = 1.6, 7.6 Hz, 1H, ArH) 6.97 (m, 1H, ArH), 5.07 (dd, *J* = 2.0, 3.4 Hz, 1H, C=CHCH₂), 4.98 (dd, *J* = 2.3, 11.0 Hz, NCHCO₂CH₃), 3.82 (s, 3H, CO₂CH₃), 3.12 (ddd, *J* = 2.0, 11.0, 17.0 Hz, 1H, C=CHCHHCH), 2.55 (dt, *J* = 2.9, 17.0 Hz, 1H, C=CHCHHCH), 2.24 (s, 3H, NHCOCH₃), 1.08 (s, 9H, C(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃) δ 173.7, 169.3, 151.4, 140.9, 136.8, 128.9, 128.4, 122.6, 122.5, 119.7, 110.2, 81.3, 60.6, 52.9, 32.3, 27.6, 24.7; HRMS (EI) calcd for C₁₉H₂₄N₂O₅ 360.1685, found 360.1682.

Methyl (2S)-2-[di(*tert*-butoxycarbonyl)amino]-3-(1*H*-2-indolyl)propanoate

(20). Following the general procedure, to a solution of **15** (327 mg, 0.78 mmol) in MeCN (12 mL), PdCl₂(MeCN)₂ (20 mg, 0.08 mmol) was added. Purification by chromatography (EtOAc/heptane = 1:6) afforded **20** (170 mg, 0.41 mmol, 52%) as

a white solid. *R*_f 0.28 (EtOAc/heptane = 1:3); mp 143.0 °C; [α]_D = −99.9 (*c* 1.0, CH₂Cl₂); IR (neat) 3392, 2983, 1743, 1726, 1685, 1456; ¹H NMR (300 MHz, CDCl₃) δ 8.45 (s, 1H, NH), 7.47 (d, *J* = 8.1 Hz, 1H, ArH), 7.24 (d, *J* = 7.7 Hz, 1H, ArH), 7.04 (m, 2H, ArH), 6.25 (d, *J* = 1.2 Hz, 1H, CH=C), 5.15 (t, *J* = 6.9 Hz, 1H, NCHCO₂CH₃), 3.75 (s, 3H, CO₂CH₃), 3.61 (dd, *J* = 6.6, 15.0 Hz, 1H, CHCHHC=C), 3.28 (dd, *J* = 7.2, 15.0 Hz, 1H, CHCHHC=C), 1.40 (s, 18H, 2 x C(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃) δ 171.1, 151.7, 136.1, 134.9, 128.5, 121.2, 119.9, 119.5, 110.6, 101.8, 83.6, 58.4, 52.7, 30.1, 28.2; HRMS (EI) calcd for C₂₂H₃₀N₂O₆ 418.2104, found 418.2105.

Methyl (2S)-2-[(*tert*-butoxycarbonyl)amino]-4-(1*H*-2-indolyl)butanoate (23).

Following the general procedure, to a solution of **22** (556 mg, 1.67 mmol) in MeCN (16 mL), PdCl₂(MeCN)₂ (43 mg, 0.17 mmol) was added. Purification by chromatography (EtOAc/heptane = 1:4) afforded **23** (334 mg, 1.00 mmol, 60%) as a light-brown oil. *R*_f 0.14 (EtOAc/heptane = 1:3); [α]_D = −26.8 (*c* 0.5, CH₂Cl₂); IR (neat) 3381, 2954, 1693, 1504, 1454; ¹H NMR (300 MHz, CDCl₃) δ 9.15 (br s, 1H, NH (indolyl)), 7.50 (d, *J* = 7.5 Hz, 1H, ArH), 7.32 (d, *J* = 7.8 Hz, 1H, ArH), 7.12–7.00 (m, 2H, ArH), 6.22 (s, 1H, CH=C), 5.22 (br d, *J* = 8.1 Hz, 1H, NH), 4.43 (br m, 1H, NHCHCO₂CH₃), 3.67 (s, 3H, CO₂CH₃), 2.92–2.72 (m, 2H, CH₂CH₂C=C), 2.19–2.08 (m, 1H, CHCHHCH₂), 1.99–1.87 (m, 1H, CHCHHCH₂), 1.47 (s, 9H, C(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃) δ 172.7, 155.9, 138.2, 136.0, 128.6, 121.0, 119.7, 119.4, 110.8, 99.9, 80.7, 52.8, 52.7, 34.5, 28.6, 24.3; HRMS (EI) calcd for C₁₈H₂₄N₂O₄ 332.1736, found 332.1727.

Methyl (2S)-2-[(*tert*-butoxycarbonyl)amino]-5-(1*H*-2-indolyl)pentanoate (26**).**

Following the general procedure, to a solution of **25** (226 mg, 0.65 mmol) in MeCN (12 mL), PdCl₂(MeCN)₂ (17 mg, 0.07 mmol) was added. Purification by chromatography (EtOAc/heptane = 1:4) afforded **26** (125 mg, 0.36 mmol, 55%) as a light-brown oil. *R*_f 0.17 (EtOAc/heptane = 1:3); [α]_D = +5.2 (*c* 0.5, CH₂Cl₂); IR (neat) 3377, 2949, 1734, 1691, 1504, 1456; ¹H NMR (300 MHz, CDCl₃) δ 8.30 (br s, 1H, NH (indolyl)), 7.49 (d, *J* = 7.2 Hz, 1H, ArH), 7.25 (m, 1H, ArH), 7.10-7.00 (m, 2H, ArH), 6.20 (s, 1H, CH=C), 5.11 (br d, *J* = 7.2 Hz, 1H, NH), 4.40 (br m, 1H, NHCHCO₂CH₃), 3.72 (s, 3H, CO₂CH₃), 2.86-2.71 (m, 2H, CH₂CH₂C=C), 1.91-1.65 (m, 4H, CHCH₂CH₂CH₂), 1.47 (s, 9H, C(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃) δ 172.9, 155.5, 138.9, 135.9, 128.6, 120.9, 119.7, 119.4, 110.4, 99.6, 80.3, 53.0, 52.5, 32.8, 28.6, 27.5, 25.5; HRMS (EI) calcd for C₁₉H₂₆N₂O₄ 346.1893, found 346.1894.