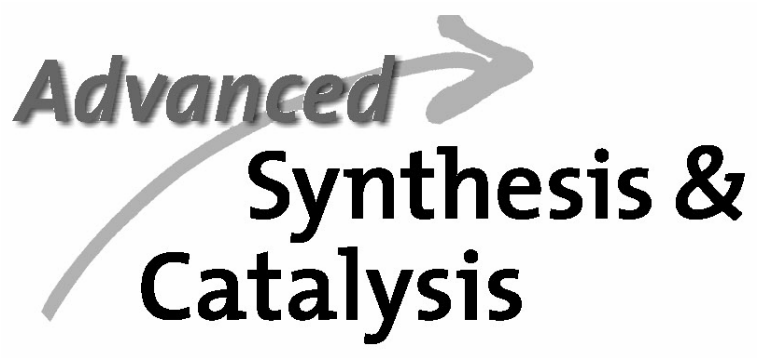

Supporting Information

Supporting information

General Remarks

NMR spectra were recorded on a Bruker spectrometer (400 MHz for ^{1}H and 101 MHz for ^{13}C) at ambient temperature in the solvents indicated, and referenced to TMS. UV-Vis spectra were recorded on a Perkin Elmer spectrometer (Lambda Bio 40). Elementary analysis was carried out on a Leco CHN-900 device. Melting points were measured on a Büchi 530 and are not corrected. Mass spectra were recorded with a VG70-250(FAB), Finnigan MAT MS 312 (EI) or Finnigan MAT LCQ (ESI) spectrometer. Optical rotations were measured on a Perkin Elmer polarimeter 241 (conc. given in g/100 mL). *ee*s were determined by chiral HPLC (Chiracel columns from Daicel). Pulsed cyclovoltammetric measurements were performed using a BAS 100 B/W electrochemical workstation and a three-electrode cell, consisting of a silver-wire as pseudo-reference, a glassy carbon disk as working and a platinum wire as counter electrode. The amino acids were dissolved in degassed acetonitrile at 2 mM concentrations. Tetrabutylammoniumhexafluorophosphate was added as an electrolyte (100 mM) and ferrocene as an internal standard. The measurements were carried out under an argon blanket. Commercially available chemicals were reagent grade and were used without further purification. The chiral Rh-catalyst was ordered from Strem. Ion exchange chromatography was performed on Dowex 400 resin activated by washing with 2 M aq. sodium hydroxide and subsequently 2 M acetic acid. Silica gel 60 (Fluka) was used for flash chromatography.

Trifluoro-methanesulfonic acid 2-(2,2-dimethylpropionyl)-3-(diphenoxyphosphoryloxy) tetrahydrofuran-2-yl methyl ester (7).

mp 96-97°C. ^{1}H-NMR ($CDCl_3$, 400 MHz): *d* = 7.39-7.32 (m, 4H; H_{Ar}), 7.27-7.17 (m, 6H; H_{Ar}), 5.17-5.12 (m, 1H; C*H*CH_2), 4.71 (d, *J* = 11.4 Hz, 1H; CH*H*OTf), 4.32 (d, *J* = 11.4 Hz, 1H; C*H*HOTf), 4.28-4.15 (m, 2H; OC*H*$_2$$CH_2$), 2.30-2.20 (m, 2H; OCH_2C*H*$_2$), 1.18 (s, 9H; $C(CH_3)_3$); ^{13}C-NMR (101 MHz, $CDCl_3$): *d* = 212.3 (s, C=O, *C*O*t*Bu), 150.6 (d, $J_{C\text{-}P}$ = 6.9 Hz, C_{Ar}-OP), 150.5 (d, $J_{C\text{-}P}$ = 7.3 Hz, C_{Ar}-OP), 130.3 (d, 2 *p*-CH_{Ar}(PhOP)), 126.2 (d, 2 *m*-CH_{Ar}(PhOP)), 126.0 (d, 2 *m*-CH_{Ar}(PhOP)), 120.5 (d, $J_{C\text{-}P}$ = 5.0 Hz, 2 *o*-CH_{Ar}(PhOP)) 120.4 (d, $J_{C\text{-}P}$ = 5.0 Hz, 2 *o*-CH_{Ar}(PhOP)), 118.9 (q, *J* = 320 Hz, CF_3), 94.5 (d, $J_{C\text{-}P}$ = 10.0 Hz, *C*CH-OP), 83.5 (dd, $J_{C\text{-}P}$ = 5.0 Hz, *C*HCH_2), 78.3 (t, *C*$H_2OSO_2CF_3$), 69.1 (t, O*C*$H_2$$CH_2$), 45.6 (s, *C*$(CH_3)_3$), 33.7 (t, OCH_2*C*H_2), 26.0 (q, C(*C*H_3)$_3$); MS (FAB, NBA): *m/z* (%): 367 ([*M*+1]$^{+}$, 52), 251 (100), 77 (18), 57 (70).

2-*tert*-Butoxycarbonylamino-3-(4-hydroxy-2-methoxy-phenyl)-propionic acid methyl ester (8).

1. 2-Amino-3-(4-hydroxy-2-methoxy-phenyl)-propionic acid methyl ester
mp 128-130°C. ^{1}H-NMR (MeOD, 400 MHz): *d* = 6.92 (d, *J* = 8.4 Hz, 1H; H_{Ar}-6(Tyr-OCH_3)), 6.46 (d, *J* = 2.3 Hz, 1H; H_{Ar}-3(Tyr-OCH_3)), 6.36 (dd, *J* = 8.4, 2.3 Hz, 1H; H_{Ar}-5(Tyr-OCH_3)), 4.21 (dd, *J* = 7.3, 5.6 Hz, 1H; C_aH), 3.81 (s, 3H; CO_2CH_3), 3.78 (s, 3H; C_{Ar}-OCH_3), 3.21 (dd, *J* = 14.4, 5.6 Hz, 1H; C_aHC*H*H), 2.99 (dd, *J* = 14.4, 7.3 Hz, 1H; C_aHCH*H*); ^{13}C-NMR (101 MHz, MeOD, 25°C): *d* = 168.1 (s, C=O, *C*O_2CH_3), 157.7, 157.3 (2s, *C*$_{Ar}$-OCH_3, C_{Ar}-OH), 130.3 (d, *C*H_{Ar}-6(Tyr-OCH_3)), 111.8 (s, *C*$_{Ar}$-CH_2), 105.7 (d, *C*H_{Ar}-5(Tyr-OCH_3)), 97.5 (d, *C*H_{Ar}-3(Tyr-OCH_3)), 53.2 (q, C_{Ar}-OCH_3), 51.9 (d, C_αH), 50.9 (q, CO_2*C*H_3), 29.6 (t, C_αH*C*H_2); MS (FAB, NBA): *m/z* (%): 226 ([*M*]$^+$, 100), 212 (62), 137 (32).
2.
mp 103-105°C. ^{1}H-NMR ($CDCl_3$, 400 MHz): *d* = 6.90 (d, *J* = 7.8 Hz, 1H; H_{Ar}-6(Tyr-OCH_3)), 6.37 (d, *J* = 2.3 Hz, 1H; H_{Ar}-3(Tyr-OCH_3)), 6.33 (dd, *J* = 7.8, 2.3 Hz, 1H; H_{Ar}-5(Tyr-OCH_3)), 5.18 (d, *J* = 11.4, 1H; NH), 4.44 (m, 1H; C_aH), 3.77 (s, 3H; CO_2CH_3), 3.70 (s, 3H; C_{Ar}-OCH_3), 2.97 (m, 2H; C_aHC*H*$_2$), 1.39 (s, 9H; $CO_2C(CH_3)_3$); ^{13}C-NMR (101 MHz, $CDCl_3$, 25°C): *d* = 172.1 (s, C=O, *C*O_2CH_3), 159.8 (s, *C*$_{Ar}$-OCH_3), 155.5 (s, C_{Ar}-OH), 151.7 (s, C=O, *C*$O_2C(CH_3)_3$), 131.6 (d, *C*H_{Ar}-6(Tyr-OCH_3)), 120.5 (s, *C*$_{Ar}$-CH_2), 112.5 (d, *C*H_{Ar}-5(Tyr-OCH_3)), 108.4 (d, *C*H_{Ar}-3(Tyr-OCH_3)), 84.1 (s, *C*$(CH_3)_3$), 55.8 (q, C_{Ar}-OCH_3), 54.0 (d, C_aH), 52.7 (q, CO_2*C*H_3), 32.2 (t, C_aH*C*H_2), 28.6 (q, C(*C*$H_3)_3$); MS (ESI, MeOH): *m/z* (%): 348 ([*M*+Na]$^+$, 24), 673 ([2*M*+Na]$^+$, 9), 683 (30), 741 (100).

2-*tert*-Butoxycarbonylamino-3-{4-[2-(2,2-dimethylpropionyl)-3-(diphenoxyphosphoryl-oxy)tetrahydrofuran-2-ylmethoxy]-2-methoxyphenyl}propionic acid methyl ester (9).

mp 47-49°C. ^{1}H-NMR ($CDCl_3$, 400 MHz): *d* = 7.39-7.31 (m, 4H; H_{Ar}(PhOP)), 7.27-7.16 (m, 6H; H_{Ar}(PhOP)), 6.95 (d, *J* = 7.8 Hz, 1H; H_{Ar}-6(Tyr-OCH_3)), 6.36-6.31 (m, 2H; H_{Ar}-3(Tyr-OCH_3), H_{Ar}-5(Tyr-OCH_3)), 5.35-5.31 (m, 1H; CH-OP), 5.19-5.11 (br, 1H; NH), 4.49-4.38 (m, 1H; C_a*H*CH_2,), 4.31-4.09 (m, 4H; OCH_2CO, O*C*H_2CH_2), 3.78, (s, 3H; C_{Ar}-OCH_3), 3.68 (s, 3H; CO_2CH_3), 3.03-2.84 (m, 2H; C_aHC*H*$_2$), 2.50-2.38 (m, 1H; OCH_2C*H*H), 2.28-2.20 (m, 1H; OCH_2CH*H*), 1.39, 1.22 (2s, 2 x 9H, 2C(C*H*$_3)_3$); ^{13}C-NMR (101 MHz, $CDCl_3$): *d* = 213.0 (s, C=O; *C*O*t*Bu), 172.1 (s, C=O, *C*O_2CH_3), 159.2 (s, *C*$_{Ar}$-OCH_3), 158.9 (s, C=O, NH*C*O_2*t*Bu), 155.6 (s, *C*$_{Ar}$-OCH_2), 150.8 (d, $J_{C\text{-}P}$ = 7.3 Hz, C_{Ar}-OP), 150.7 (d, $J_{C\text{-}P}$ = 7.3 Hz, C_{Ar}-OP), 131.9 (d, *C*H_{Ar}-6(Tyr-OCH_3)), 130.2 (d, 2 *p*-CH_{Ar}(PhOP)), 126.2 (d, 2 *m*-CH_{Ar}(PhOP)), 126.0 (d, 2 *m*-CH_{Ar}(PhOP)), 120.6 (d, $J_{C\text{-}P}$ = 5.0 Hz, 2 *o*-CH_{Ar}(PhOP)) 120.5 (d, $J_{C\text{-}P}$ = 5.0 Hz, 2 *o*-

CH_{Ar}(PhOP)), 118.1 (s, C_{Ar}-CH_2), 105.3 (d, CH_{Ar}-6(Tyr-OCH_3)), 99.2 (s, CH_{Ar}-3(Tyr-OCH_3)), 96.8, 96.7 (s, O*C*CHCH$_2$), 84.8 (dd, $J_{C\text{-}P}$ = 5.7 Hz, C*C*HCH$_2$), 79.9 (s, O*C*(*C*H$_3$)$_3$), 73.4 (t, O*C*H$_2$CH$_2$), 68.4 (t, *C*H$_2$OC_{Ar}), 55.8 (q, C_{Ar}-O*C*H$_3$), 54.5 (d, C$_?$H), 52.4 (q, CO_2*C*H$_3$), 45.8 (s, *C*(CH$_3$)$_3$), 34.2 (t, C_aH*C*H$_2$), 32.6 (t, OCH$_2$*C*H$_2$), 28.7 (q, C(*C*H$_3$)$_3$), 26.0 (q, C(*C*H$_3$)$_3$); MS (ESI): *m/z* (%) : 764 ([*M*+Na]$^+$, 100); MS (FAB, NBA): *m/z* (%): 780 ([*M*–H+K]$^+$, 11), 642 (23), 553 (15), 251 (23), 167 (19), 57 (100); EA: calc. for $C_{38}H_{48}NO_{12}P$: C: 61.53, H: 6.52, N: 1.89; found C: 61.37, H: 6.51, N: 1.60.

4-(2´-Methoxy-4´-acetoxybenzylidene)-2-phenyloxazol-5(4*H*)-one (10).

mp 188-189°C. ^{1}H-NMR ($CDCl_3$, 400 MHz): *d* = 8.90 (d, *J* = 8.6 Hz, 1H; H_{Ar}-6(Tyr-OCH_3)), 8.19-8.12 (m, 2H; H_{Ar}-2`, 6`), 7.77 (s, 1H; CH), 7.62-7.56 (m, 1H; H_{Ar}-4`), 7.55-7.48 (m, 2H; $H_{Ar}$-3`, 5`), 6.85 (dd, *J* = 8.6, 2.0 Hz, 1H; H_{Ar}-5(Tyr-OCH_3)), 6.70 (d, *J* = 2.0 Hz, 1H; H_{Ar}-3(Tyr-OCH_3)), 3.89 (s, 3H; CH_3CO_2), 2.33 (s, 3H; C_{Ar}-OCH_3); ^{13}C-NMR ($CDCl_3$, 101 MHz): *d* = 168.9 (s, C=O, COCN), 167.8 (s, C=O, CH_3CO_2), 163.0 (s, C=N), 160.1 (s, *o*-C_{Ar}-OCH_3), 154.2 (s, *p*-C_{Ar}-OAc), 133.8 (d, *C*H=C), 133.1 (d, *p*-CH_{Ar}), 132.3 (s, C_{Ar}), 128.9 (d, 2*o*-CH_{Ar}), 128.2 (d, 2*m*-CH_{Ar}), 125.7 (s, CH=*C*), 124.9 (d, *C*H$_{Ar}$-6(Tyr-OCH_3)), 120.3 (s, C_{Ar}-CH), 114.2 (d, *C*H$_{Ar}$-5(Tyr-OCH_3)), 104.7 (d, *C*H$_{Ar}$-3(Tyr-OCH_3)), 55.8 (q, CH_3-O), 21.2 (q, CH_3CO_2); MS (EI, 70 eV, 200 °C): *m/z* (%) = 337 (13), 295 (35), 105 (100), 77 (26); EA: calc. for $C_{19}H_{15}NO_5 \cdot {}^1/_3\ H_2O$: C: 66.47, H: 4.60, N: 4.08; found C: 66.54, H: 4.50, N: 4.12.

2-Benzoylamino-3-(4-hydroxy-2-methoxyphenyl)-acrylic acid methyl ester (11)

mp 207-208°C. ^{1}H-NMR ($CDCl_3$/DMSO = 30:1, 400 MHz): *d* = 8.82 (s, 1H; NH), 7.97-7.89 (m, 2H; 2*o*-H_{Ar}(CONHPh)), 7.67 (s, 1H; CH=C), 7.57-7.51 (m, 1H; *p*-H_{Ar}(CONHPh)), 7.50-7.42 (m, 3H; 2*m*-H_{Ar}(CONHPh), H_{Ar}-6(Tyr-OCH_3)), 6.43 (d, *J* = 2.3 Hz, 1H; H_{Ar}-3(Tyr-OCH_3)), 6.39 (dd, *J* = 8.6, 2.3 Hz, 1H; H_{Ar}-5(Tyr-OCH_3)), 3.84 (s, 3H; CO_2CH_3), 3.81 (s, 3H; C_{Ar}-OCH_3); ^{13}C-NMR ($CDCl_3$/DMSO = 30:1, 101 MHz): *d* = 165.9 (s, C=O, *C*$O_2$$CH_3$), 165.7 (s, C=O, *C*ONHPh), 160.1 (s, C_{Ar}-OCH_3), 158.6 (s, C_{Ar}-OH), 133.4 (s, C_{Ar}-CONHPh), 131.3, 130.5 (d, *C*H$_{Ar}$-6(Tyr-OCH_3), *p*-*C*H$_{Ar}$(CONHPh)), 128.0 (d, 2*m*-*C*H$_{Ar}$(CONHPh)), 127.6 (d, C=*C*H), 127.2 (d, 2*o*-*C*H$_{Ar}$(CONHPh)), 122.4 (s, *C*=CH), 113.4 (s, C_{Ar}-CH), 107.7 (d, *C*H$_{Ar}$-5(Tyr-OCH_3)), 98.7 (d, *C*H$_{Ar}$-3(Tyr-OCH_3)), 55.2 (q, C_{Ar}-O*C*H$_3$), 51.8 (q, CO_2*C*H$_3$); MS (EI, 70 eV, 250 °C): *m/z* (%) = 327 (47), 190 (21), 163 (8), 148 (8), 105 (100), 77 (33); EA: calc. for $C_{18}H_{17}NO_5$: C: 66.05, H: 5.23, N: 4.28; found C: 65.86, H: 5.23, N: 4.30.

2-(*S*)-Benzoylamino-3-(4-hydroxy-2-methoxyphenyl)-propionic acid methyl ester (12).

mp 206-208°C. $[\alpha]_D^{20}$ = +21.2 $cm^3g^{-1}dm^{-1}$ (c = 0.73 in $CHCl_3$); ^{1}H-NMR ($CDCl_3$, 400 MHz): *d* = 7.74-7.67 (m, 2H; 2*o*-H_{Ar}(CONHPh)), 7.52-7.45 (m, 1H; *p*-H_{Ar}(CONHPh)), 7.43-7.36 (m, 2H; 2*m*-H_{Ar}(CONHPh)), 7.12 (d, *J* = 7.1 Hz, 1H; NH), 6.90 (d, *J* = 8.1 Hz, 1H; H_{Ar}-6(Tyr-OCH_3)), 6.36 (d, *J* = 2.3 Hz, 1H; H_{Ar}-3(Tyr-OCH_3)), 6.32 (dd, *J* = 8.1, 2.3 Hz, 1H; H_{Ar}-5(Tyr-OCH_3)), 4.87 (dd, *J* = 7.0, 6.2 Hz, 1H; C_aH), 3.74 (s, 3H; CO_2CH_3), 3.72 (s, 3H; C_{Ar}-OCH_3), 3.16-3.11 (m, 2H; C_aHCH_2); ^{13}C-NMR ($CDCl_3$, 101 MHz): *d* = 172.5 (s, C=O, CO_2CH_3), 167.4 (s, C=O, *C*ONHPh), 158.3 (s, C_{Ar}-OCH_3), 156.8 (s, C_{Ar}-OH), 133.8 (s, C_{Ar}-CONHPh), 131.73, 131.66 (d, CH_{Ar}-6(Tyr-OCH_3), *p*-CH_{Ar}(CONHPh)), 128.5 (d, 2*m*-CH_{Ar}(CONHPh)), 127.0 (d, 2*o*-CH_{Ar}(CONHPh)), 115.9 (s, C_{Ar}-CH), 107.5 (d, CH_{Ar}-5(Tyr-OCH_3)), 99.2 (d, CH_{Ar}-3(Tyr-OCH_3)), 55.4 (q, C_{Ar}-OCH_3), 54.2 (d, C_aH), 52.3 (q, CO_2CH_3), 31.7 (t, CH_2); MS (FAB, NBA): *m/z* (%): 330 ([*M*+1]$^+$, 100), 270 (24), 208 (30), 105 (37); EA: calc. for $C_{18}H_{19}NO_5$: C: 65.64, H: 5.81, N: 4.25; found C: 65.33, H: 5.93, N: 4.27.

2-(*S*)-Amino-3-(4-hydroxy-2-methoxyphenyl)-propionic acid (13). ("4-Hydroxy-2-phenylalanine")

mp 166-168°C. $[\alpha]_D^{20}$ = - 32.4 $cm^3g^{-1}dm^{-1}$ (c = 0.11 in H_2O); ^{1}H-NMR (D_2O, 400 MHz): *d* = 7.04 (d, *J* = 8.2 Hz, 1H; H_{Ar}-6(Tyr-OCH_3)), 6.53 (d, *J* = 2.3 Hz, 1H; H_{Ar}-3(Tyr-OCH_3)), 6.45 (dd, *J* = 8.2, 2.3 Hz, 1H; H_{Ar}-5(Tyr-OCH_3)), 3.92 (dd, *J* = 8.0, 4.7 Hz, 1H; C_aH), 3.80 (s, 3H; OCH_3), 3.23 (dd, *J* = 14.5, 4.7 Hz, 1H; C_aHCHH), 2.92 (dd, *J* = 14.5, 8.0 Hz, 1H; C_aHCHH); ^{13}C-NMR (D_2O/$MeOH_{trace}$, 101 MHz): *d* = 174.8 (s, C=O, CO_2H), 159.2 (s C_{Ar}-OCH_3), 157.1 (s, C_{Ar}-OH), 132.8 (d, CH_{Ar}-6(Tyr-OCH_3)), 115.7 (s, C_{Ar}-CH_2), 108.0 (d, CH_{Ar}-5(Tyr-OCH_3)), 99.9 (d, CH_{Ar}-3(Tyr-OCH_3)), 56.1 (d, C_aH), 55.9 (q, OCH_3), 31.4 (t, CH_2); MS (FAB, NBA): *m/z* (%): 365 ([*M*+NBA+H]$^+$, 5), 212 ([*M*+H]$^+$, 100), 166 (22), 137 (43); MS (EI, 70 eV, 200 °C): *m/z* (%): 211 ([*M*]$^+$, 1), 137 ([2-OMe,4-OH-$PhCH_2$]$^+$, 100), 107 (34), 77 (9); EA: calc. for $C_{10}H_{13}NO_4.{}^1/_3\ H_2O$: C: 55.29, H: 6.34, N: 6.45; found C: 55.21, H: 6.64, N: 6.39.

4-[1-(2,4-Dimethoxy-phenyl)-meth-(*Z*)-ylidene]-2-phenyl-4*H*-oxazol-5-one (15).

mp 161-163°C. ^{1}H-NMR (MeOD, 400 MHz): *d* = 8.90 (d, *J* = 8.8 Hz, 1H; H_{Ar}-6), 8.17-8.14 (m, 2H; H_{Ar}-2`, 6`), 7.81 (s, 1H; CH), 7.61-7.47 (m, 3H; H_{Ar}-3`, 4`, 5`), 6.66 (dd, *J* = 8.8, 2.3 Hz, 1H; H_{Ar}-5), 6.45 (d, *J* = 2.3 Hz, 1H; H_{Ar}-3), 3.89 (s, 6H; $2CH_3$-O); ^{13}C-NMR (MeOH, 101 MHz): *d* = 168.7 (s, C=O), 164.5 (s, C=N), 161.5 (s, *p*C_{Ar}-OCH_3), 161.0 (s, *o*C_{Ar}-OCH_3), 134.1 (s, C_{Ar}), 133.1 (d, CH_{Ar}), 130.6 (d, CH_{Ar}), 129.2 (d, $2CH_{Ar}$), 128.4 (d, $2CH_{Ar}$), 126.7 (d, *C*H=C), 123.2 (s, CH=*C*), 116.6 (s, C_{Ar}), 106.7 (d, CH_{Ar}), 98.1 (d, CH_{Ar}), 56.0, 56.1 (q, $2CH_3$-O); MS (EI, 70 eV, m/z): 309 ([*M*]$^+$, 30), 206 (64), 105 (100), 77 (25); EA: calc. for $C_{20}H_{21}NO_6$: C: 69.89, H: 4.89, N: 4.53; found C: 69.63, H: 4.92, N: 4.40.

2-Phenyl-4-[1-(2,4,6-trimethoxy-phenyl)-meth-(Z)-ylidene]-4*H*-oxazol-5-one (16).

mp 150-152°C. ^{1}H-NMR ($CDCl_3$, 400 MHz): *d* = 8.06 (d, *J* = 7.6 Hz, 2H; H_{Ar}-2`, 6`), 7.57-7.43 (m, 3H; H_{Ar}-3`, 4`, 5`), 7.47 (s, 1H; CH), 6.15 (s, 2H; H_{Ar}-3, 5), 3.87, 3.86, 3.84 (s, 9H; $3CH_3$-O); ^{13}C-NMR ($CDCl_3$, 101 MHz): *d* = 168.6 (s, C=O), 164.7 (s, C=N), 161.2 (s, *p*C_{Ar}-OCH_3), 161.0 (s, 2*o*C_{Ar}-OCH_3), 132.9 (d, CH_{Ar}), 129.1 (d, $2CH_{Ar}$), 128.3 (d, $2CH_{Ar}$), 126.9 (d, C=*C*H), 126.8 (s, *C*=CH), 105.9 (s, C_{Ar}), 91.3 (d, $2CH_{Ar}$), 56.3, 55.9 (q, $3CH_3$-O); MS (EI, 70 eV, m/z): 339 ([*M*]$^+$, 36), 206 (64), 105 (100), 77 (24); HR-MS (ESI): m/z=362.0997, calcd. for $C_{19}H_{17}NO_5$ (M+Na): 362.1107.

(Z)-2-Benzoylamino-3-(2,4-dimethoxy-phenyl)-acrylic acid methyl ester (17)

mp 136-138°C. ^{1}H-NMR ($CDCl_3$, 400 MHz): *d* = 8.07 (s, 1H; NH), 7.85 (d, *J* = 7.4 Hz, 2H; H_{Ar}-2`, 6`), 7.57 (s, 1H; CH), 7.51 (d, *J* = 7.6 Hz, 1H; H_{Ar}-6), 7.48-7.40 (m, 3H; H_{Ar}-3`, 4`, 5`), 6.45-6.40 (m, 2H; H_{Ar}-3, 5), 3.87, 3.84, 3.79 (s, 9H; $3CH_3$-O); ^{13}C-NMR ($CDCl_3$, 101 MHz): *d* = 166.5 (s, C=O, *C*O_2Me), 165.8 (s, C=O, *C*OPh), 162.4 (s, *p*C_{Ar}-OCH_3), 158.9 (s, *o*C_{Ar}-OCH_3), 134.3 (s, C_{Ar}), 132.4 (d, CH_{Ar}), 131.5 (d, CH_{Ar}), 129.1 (d, $2CH_{Ar}$), 127.8 (d, $2CH_{Ar}$), 126.5 (d, *C*H=C), 123.9 (s, CH=*C*), 116.2 (s, C_{Ar}) , 105.7 (d, CH_{Ar}), 99.1 (d, CH_{Ar}), 56.3, 55.8, 53.0 (q, $3CH_3$-O); MS (ESI, m/z): 364 ([*M*+Na]$^+$, 100) ; EA: calc. for $C_{20}H_{21}NO_6$: C: 66.85, H: 5.61, N: 4.10; found C: 66.95, H: 5.53, N: 4.03.

(Z)-2-Benzoylamino-3-(2,4,6-trimethoxy-phenyl)-acrylic acid methyl ester (18).

mp 141-143°C. ^{1}H-NMR ($CDCl_3$, 400 MHz): *d* = 8.54 (s, 1H; NH), 7.80 (d, *J* = 7.6 Hz, 2H; H_{Ar}-2`, 6`), 7.51-7.40 (m, 3H; H_{Ar}-3`, 4`, 5`), 7.32 (s, 1H; CH), 6.15 (s, 2H; H_{Ar}-3, 5), 3.86 (s, 6H; $2CH_3$-O, $COOCH_3$), 3.81 (s, 3H; CH_3-O); ^{13}C-NMR (MeOH, 101 MHz): *d* = 166.1 (s, C=O, *C*O_2Me), 165.3 (s, C=O, *C*OPh), 162.7 (s, *p*-*C*$_{Ar}$-OCH_3), 159.0 (s, *o*-2*C*$_{Ar}$-OCH_3), 134.6 (s, C_{Ar}), 132.1 (d, CH_{Ar}), 128.9 (d, $2CH_{Ar}$), 127.7 (d, $2CH_{Ar}$), 126.7 (s, *C*=CH), 121.7 (d, C=*C*H), 105.6 (s, C_{Ar}) , 91.5 (d, $2CH_{Ar}$), 56.6, 55.8, 52.8 (q, $4CH_3$-O); MS (ESI, m/z): 394 ([*M*+Na]$^+$, 100); EA: calc. for $C_{20}H_{21}NO_6$: C: 64.68, H: 5.70, N: 3.77; found C: 64.67, H: 5.57, N: 3.72.

2-Benzoylamino-3-(2,4-dimethoxy-phenyl)-propionic acid methyl ester (19).

mp 97-99°C. $[\alpha]_D^{20}$ = +17.5 $cm^3g^{-1}dm^{-1}$ (c = 1.38 in CH_2Cl_2) ^{1}H-NMR (MeOD, 400 MHz): *d* = 7.70 (d, *J* = 6.8 Hz, 2H; H_{Ar}-2`, 6`), 7.52-7.45 (m, 1H; H_{Ar}-4`), 7.42-7.37 (m, 2H; $H_{Ar}$-3`, 5`), 7.03 (d, *J* = 8.1 Hz, 2H; H_{Ar}-6), 6.47-6.40 (m, 2H; H_{Ar}-3, 5), 4.85 (dd, *J* = 13.1, 6.3 Hz, 1H;

$C_\alpha H$), 3.80, 3.78, 3.74 (s, 9H; $3CH_3$-O), 3.17 (d, *J* = 6.3 Hz, 2H; $C_\alpha HCH_2$); ^{13}C-NMR (MeOH, 101 MHz): *d* = 172.4 (s, C=O, CO_2Me), 167.0 (s, C=O, *C*OPh), 160.2 (s, oC_{Ar}-OCH_3), 158.3 (s, pC_{Ar}-OCH_3), 134.1 (s, C_{Ar}), 131.7 (d, CH_{Ar}), 131.6 (d, CH_{Ar}), 128.5 (d, $2CH_{Ar}$), 127.0 (d, $2CH_{Ar}$), 116.9 (s, C_{Ar}), 104.6 (d, CH_{Ar}), 98.7 (d, CH_{Ar}), 55.5, 55.4, 52.2 (q, $3CH_3$-O), 54.1 (d, $C_\alpha H$), 31.6 (t, CH_2); MS (ESI, m/z): 366 ([*M*+Na]$^+$, 100); EA: calc. for $C_{20}H_{21}NO_6$: C: 66.46, H: 6.16, N: 4.08; found C: 66.65, H: 5.95, N: 4.03.

2-Benzoylamino-3-(2,4,6-trimethoxy-phenyl)-propionic acid methyl ester (20).

mp 147-149°C. $[\alpha]_D^{20}$ = - 38.7 $cm^3g^{-1}dm^{-1}$ (c = 0.99 in H_2O) ^{1}H-NMR (MeOD, 400 MHz): *d* = 6.15 (d, *J* = 8.6 Hz, 2H; H_{Ar}-2`, 6`), 5.99-5.87 (m, 3H; H_{Ar}-3`, 4`, 5`), 4.64 (s, 2H; H_{Ar}-3, 5), 3.06 (dd, *J* = 8.6 Hz, *J* = 5.8 Hz, 1H; $C_\alpha H$), 2.24, 2.21, 2.15 (s, 12H; $4CH_3$-O), 1.65 (dd, *J* = 13.4 Hz, *J* = 5.8 Hz, 1H; $C_\alpha HCHH$), 1.54 (dd, *J* = 13.4 Hz, *J* = 8.6 Hz, 1H; $C_\alpha HCHH$); ^{13}C-NMR (MeOH, 101 MHz): *d* = 171.7 (s, C=O, CO_2Me), 167.3 (s, C=O, *C*OPh), 159.6 (s C_{Ar}-OCH_3), 157.9 (s, $2C_{Ar}$-OCH_3), 132.6 (s, C_{Ar}), 130.4 (d, CH_{Ar}), 127.1 (d, $2CH_{Ar}$), 125.6 (d, $2CH_{Ar}$), 103.6 (s, C_{Ar}), 89.0 (d, $2CH_{Ar}$), 53.7, 53.2, 50.1 (q, $4CH_3$-O), 52.4 (d, $C_\alpha H$), 22.9 (t, CH_2); MS (ESI, m/z): 396 ([*M*+Na]$^+$, 100); HR-MS (ESI): m/z=396.1413, calcd. for $C_{20}H_{23}NO_6$ (M+Na): 396.1525.

2-Amino-3-(2,4-dimethoxy-phenyl)-propionic acid (21). ("2,4-Dimethoxyphenylalanine")

mp 228-230°C. $[\alpha]_D^{20}$ = -36.5 $cm^3g^{-1}dm^{-1}$ (c=1.02 in MeOH); ^{1}H-NMR (MeOD, 400 MHz): *d* = 5.53 (d, *J* = 8.1 Hz, 1H; H_{Ar}-6), 4.96 (s, 1 H_{Ar}-3), 4.89 (dd, *J* = 8.1, 2.0 Hz, 1H; H_{Ar}-5), 2.26 (s, 3H; O-CH_3), 2.25-2.18 (m, 1H; $C_\alpha H$), 2.19 (s, 3H; CH_3-O), 1.28 (dd, *J* = 13.6, 4.52 Hz, 2H; $C_\alpha HCH_2$); ^{13}C-NMR (MeOD, 101 MHz): *d* = 171.5 (s, C=O, CO_2H), 159.6 (s, *p*-C_{Ar}-OCH_3), 157.5 (s, *o*-C_{Ar}-OCH_3), 130.3 (d, CH_{Ar}-6), 114.9 (s, C_{Ar}-CH_2), 103.3 (d, CH_{Ar}-5), 97.0 (d, CH_{Ar}-3), 54.5 (d, $C_\alpha H$), 53.2(q, 2 CH_3-O), 30.2 (t, $C_\alpha HCH_2$); MS (FAB, NBA m/z): 226 ([*M*+1]$^+$, 100), 209 (18), 180 (22), 151 (43); HR-MS (ESI): m/z=226.1074, calcd. for $C_{11}H_{15}NO_4$ (M+1): 226.1001.

2-Amino-3-(2,4,6-trimethoxy-phenyl)-propionic acid (22). ("2,4,6-Trimethoxyphenylalanine")

mp 219-221°C. $[\alpha]_D^{20}$ = -14.1 $cm^3g^{-1}dm^{-1}$ (c=0.6 in MeOH); ^{1}H-NMR (MeOD/D_2O, 400 MHz): *d* = 4.86 (s, 2H; H_{Ar}-3, 5), 2.43 (s, 9H; 3O-CH_3), 2.30 (dd, *J* = 10.1 Hz, *J* = 3.8 Hz, 1H; $C_\alpha H$), 1.86 (dd, *J* = 13.9 Hz, *J* = 3.8 Hz, 1H; $C_\alpha HCHH$), 1.60 (dd, *J* = 13.9 Hz, *J* = 10.1 Hz, 1H; $C_\alpha HCHH$); ^{13}C-NMR (MeOH, 101 MHz): *d* = 172.4 (s, C=O, CO_2H), 159.7 (s, C_{Ar}-OCH_3),

158.2 (s, $2C_{Ar}$-OCH_3), 103.0 (s, C_{Ar}), 89.4 (d, $2CH_{Ar}$), 54.7 (d, $C_\alpha H$), 54.0, 53.8 (q, $3CH_3$-O), 23.4 (t, CH_2); MS (FAB, NBA): 256 ([*M*]$^+$, 100), 239 (21), 210 (24), 181 (52); HR-MS (ESI): m/z=256.1185, calcd. for $C_{12}H_{17}NO_5$ (M+1): 256.1107.

2-Acetyloamino-(S)-3-(2,4-dimethoxy-phenyl)-propionic acid methyl ester (23).

mp 103-105°C. ^{1}H-NMR (MeOD, 400 MHz): *d* = 6.96 (d, *J* = 8.1 Hz, 2H; H_{Ar}-6), 6.44-6.41 (m, 2H; H_{Ar}-3, 5), 4.69 (dd, *J* = 13.6, 6.3 Hz, 1H; $C_\alpha H$), 3.81, 3.79, 3.71 (s, 9H; $3CH_3$-O), 3.03 (d, *J* = 6.3 Hz, 2H; $C_\alpha HC\mathit{H}_2$), 1.93 (CH_3CO); ^{13}C-NMR (MeOH, 101 MHz): *d* = 172.9 (s, C=O, $\mathit{C}O_2Me$), 170.1 (s, C=O, $\mathit{C}OCH_3$), 160.6 (s, $o\mathit{C}_{Ar}$-OCH_3), 158.8 (s, $p\mathit{C}_{Ar}$-OCH_3), 131.9 (d, CH_{Ar}), 131.6 (d, CH_{Ar}), 117.2 (s, C_{Ar}), 104.8 (d, CH_{Ar}), 99.0 (d, CH_{Ar}), 55.8, 55.7, 52.5 (q, $3CH_3$-O), 53.7 (d, $C_\alpha H$), 32.1 (t, CH_2), 23.5 (s, $CO\mathit{C}H_3$); MS (FAB, NBA, m/z): 151 (86), 180 (24), 222 (62), 282 ([*M*]$^+$, 100); EA: calc. for $C_{14}H_{18}NO_5$: C: 59.99, H: 6.47, N: 5.00; found C: 60.03, H: 6.59, N: 5.11.

2-Acetyloamino-(S)- 3-(2,4,6-trimethoxy-phenyl)-propionic acid methyl ester (24).

mp 131-132°C. ^{1}H-NMR (MeOD, 400 MHz): *d*= 6.18 (s, 2H; H_{Ar}), 4.44 (t, *J* = 7.6 Hz, 1H; $C_\alpha H$), 3.78, 3.77, 3.63 (s, 12H; 4 x CH_3-O), 3.05 (dd, *J* = 13.2, 7.6 Hz, 1H; $C_\alpha HC\mathit{H}H$), 2.93 (dd, *J* = 13.2, 7.6 Hz, 1H; $C_\alpha HCH\mathit{H}$), 1.89 (CH_3CO); ^{13}C-NMR (MeOH, 101 MHz): *d* = 174.3 (s, C=O, $\mathit{C}O_2Me$), 173.0 (s, C=O, $\mathit{C}OCH_3$), 162.0 (s, $o\mathit{C}_{Ar}$-OCH_3), 160.5 (s, $p\mathit{C}_{Ar}$-OCH_3), 106.0 (s, C_{Ar}), 91.4 (d, $2CH_{Ar}$), 56.1, 55.7, 52.4 (q, $4CH_3$-O), 54.0 (d, $C_\alpha H$), 25.8 (t, CH_2), 22.3 (s, $CO\mathit{C}H_3$); MS (ESI, MeOH m/z): 645.0 ([2*M*+Na]$^+$, 100), 334.3 ([*M*+Na]$^+$, 24); EA: calc. for $C_{15}H_{21}NO_6$: C: 57.87, H: 6.80, N: 4.50; found C: 57.76, H: 6.64, N: 4.32.

Ac-Tyr-$(Pro)_3$-2,4-Dimethoxyphenylalanine-$(Pro)_3$-3-{4-[2-(2,2-dimethylpropionyl)-3-(diphenoxyphosphoryl-oxy)tetrahydrofuran-2-ylmethoxy]-2-methoxyphenyl}propionic acid methyl ester (25).

Purity of the compound was checked by HPLC chromatography (Merck LiChroSpher 100-5, RP-18e; acetonitrile/water 0% to 100% in 40 min) and UV-spectroscopy ($\varepsilon_{308} < 60$ $M^{-1}cm^{-1}$).
MS (ESI, MeOH m/z): (, [*M*+Na]$^+$) 1658.6
HPLC: rt 30.0'

Ac-Tyr-$(Pro)_3$-2,4,6-Trimethoxyphenylalanine-$(Pro)_3$-3-{4-[2-(2,2-dimethylpropionyl)-3-(diphenoxyphosphoryl- oxy)tetrahydrofuran-2-ylmethoxy]-2-methoxyphenyl}propionic acid methyl ester (26).

Purity of the compound was checked by HPLC chromatography (Merck LiChroSpher 100-5, RP-18e; acetonitrile/water 0% to 100% in 40 min) and UV-spectroscopy ($\varepsilon_{308} < 60\ M^{-1}cm^{-1}$).
MS (ESI, MeOH m/z): (, $[M+Na]^+$) 1688.6
HPLC: rt 30.6'

CD-spectroscopic analysis: CD spectra were recorded using a Chirascan spectrometer with a spectral bandwidth of 1 nm, at 25 °C with a time constant of 3 s and a step resolution of 1 nm. CD data are given as mean residual molar ellipticities (Θ MRW in deg $cm^2\ mol^{-1}$). A quartz cell with a path length of 1 cm was used with solutions containing approximately 20 µg mL^{-1} peptide solutions. The blank spectrum of the solvent was substracted.

Laser Flash Photolysis: The laser experiments were carried out using a COMPex 205 XeCl-Excimer Laser (Lambda Physik) with a pulse energy of 100-150 mJ and a pulse width of 20 ns. Transient absorption spectra were recorded with an iStar ICCD detector (Andor). The signals of 5 laser flashes were accumulated. The peptides were dissolved in acetonitrile/water 3:1 in concentrations of approx. 5 mM and degassed in a quartz cuvette in three freeze/thaw cycles. Photosensitization experiments were carried out in oxygen-saturated acetonitrile with 1mM concentrations of compound, 0.1 mM dicyanonapthtalene and 20 mM biphenyl.