An Efficient Synthesis of 1-Azadienes Derived from α -Aminoesters. Regioselective Preparation of α -Dehydroamino Acids, Vinylglycines and α -Amino Acids

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General. All solvents used in reactions were freshly distilled from appropriate drying agents before use. All other reagents were recrystallized or distilled as necessary. All reactions were performed under an atmosphere of dry nitrogen. ^1H (300 MHz), ^{13}C (75 MHz) and ^{31}P NMR (120 MHz) spectra were performed using CDCl_3 or CD_3OD solutions with TMS as an internal reference ($\delta = 0.00$ ppm) for ^1H and ^{13}C NMR spectra and phosphoric acid (50 %) ($\delta = 0.0$ ppm) for ^{31}P NMR spectra. Chemical shifts (δ) are reported in ppm. Coupling constants (J) are reported in Hertz. β,γ -unsaturated α -ketoesters **10**¹ and methyldiphenylphosphine oxide² were synthesized according to literature procedures.

Synthesis of the mixture ethyl 3-(diphenylphosphinoyl)-2-oxopropionate / ethyl 3-(diphenylphosphinoyl)-2-hydroxyacrylate 2. To a freshly prepared solution of LDA (12 mmol) in THF (25 mL) at -78°C was added a solution of methyldiphenylphosphine oxide (2.16 g, 10 mmol) in THF (15 mL). The resulting solution was stirred 1 h at -78°C and neat diethyl oxalate (1.63 mL, 12 mmol) was added. The solution was allowed to warm to r.t. overnight and a 1 M aqueous solution of HCl (40 mL) was then added. The resulting mixture was stirred for 1 h. at r.t. and was then extracted with CH_2Cl_2 (3×25 mL) which was washed with H_2O (50 mL), dried over MgSO_4 and concentrated under reduced pressure, affording 2.56 (81 %) of the crude mixture ketone / enol tautomers (60 / 40)³ as a sticky pale yellow oil. R_f (AcOEt): 0.16. ^1H NMR (300 MHz, CDCl_3): δ 12.1 (s, 0.4 $\times$ 1 H), 7.73–7.39 (m, 10 H, 10 CH ketone and enol), 5.86 (d, $^2J_{\text{PH}} = 19.8$ Hz, 0.4 $\times$ 1 H, CH= enol), 4.27 (q, $^3J_{\text{HH}} = 7.2$ Hz, 0.4 $\times$ 2 H enol), 4.09 (q, $^3J_{\text{PH}} = 7.1$ Hz, 0.6 $\times$ 2 H, ketone), 4.03 (d, $^2J_{\text{PH}} = 15.1$ Hz, 0.6 $\times$ 2 H ketone), 1.28 (t, $^3J_{\text{HH}} = 7.2$ Hz, 0.4 $\times$ 3 H enol), 1.18 (t, $^3J_{\text{HH}} = 7.1$ Hz, 0.6 $\times$ 3 H ketone). ^{13}C RMN: δ 186.3 (d, $^2J_{\text{PC}} = 6.0$ Hz ketone), 161.1 (d, $^2J_{\text{PC}} = 17.1$ Hz enol), 159.3 (ketone), 158.9 (enol), 131.7–127.6 (m, ketone and enol), 91.6 (d, $^1J_{\text{PC}} = 102.2$ Hz enol), 62.0 (ketone), 61.4 (enol), 41.4 (d, $^1J_{\text{PC}} = 56.9$ Hz ketone), 13.2 (enol), 12.9 (ketone). ^{31}P RMN:

¹ (a) Palacios, F.; Vicario, J.; Aparicio, D. *Eur. J. Org. Chem.* **2006**, 2847. (b) N. Halland, T. Velgaard, K.A. Jørgensen, *J. Org. Chem.* **2003**, 68, 5067.

² N.J. Lawrence in "Preparation of Alkenes", J. M. J. Williams Ed. Oxford, 1996.

³ Determined by the integration of the ^{31}P NMR signals.

δ 35.7 (enol), 26.1 (ketone). FTIR (KBr) $\nu_{\max}$ (cm⁻¹): 3436, 1778, 1719. EIMS m/z (amu): 316 (M⁺, 35), 243 (100), 115 (71).

Synthesis of ethyl *E*-3-(diphenylphosphinoyl)-2-*p*-tolylaminoacrylate 1. A solution of ketone enol

mixture (5 mmol) and *p*-toluidine (536 mg, 5 mmol) in toluene (20 mL) was stirred and refluxed for 3 h. with a Dean-Stark and the resulting mixture was then cooled to r.t. and concentrated under reduced pressure. The crude residue was

purified by crystallization from Et₂O, affording 1.44 g (69 %) of **5a** as a white solid. M.p. 139–140 °C (Et₂O). ¹H NMR (300 MHz, CDCl₃): δ 9.25 (s, 1 H), 7.70–7.64 (m, 5 H), 7.46–7.40 (m, 5 H), 6.96 (d, ³*J*_{HH} = 7.8 Hz, 2 H), 6.71 (d, ³*J*_{HH} = 7.8 Hz, 2 H), 5.25 (d, ²*J*_{PH} = 20.3 Hz, 1 H), 4.06 (q, ³*J*_{HH} = 7.0 Hz, 2 H), 2.21 (s, 3 H), 1.00 (t, ³*J*_{HH} = 7.0 Hz, 1 H). ¹³C RMN: δ 164.7 (d, ³*J*_{PC} = 17.5 Hz), 150.3, 138.9, 134.6–130.1 (m), 120.2, 92.0 (d, ¹*J*_{PC} = 104.8 Hz), 61.8, 20.6, 13.5. ³¹P RMN: δ 29.4. FTIR (KBr) $\nu_{\max}$ (cm⁻¹): 3250, 1725. EIMS m/z (amu): 405 (M⁺, 65), 204 (100). % Elem. Anal. Calcd. for C₂₄H₂₄NO₃P: C 71.10, H 5.97, N 3.45. Found: C 71.05, H 5.94, N 3.48.

Wittig-Horner reaction of phosphorated enamine 1 with *p*-nitrobenzaldehyde 3a. To a suspension of NaH (120 mg, 5 mmol) in THF (20 mL) at 0 °C was added a solution of enamine **1** (1.22 g, 3 mmol) in THF (10 mL). The mixture was allowed to stir at this temperature for 1 h. and a solution of *p*-nitrobenzaldehyde (414 mg, 3 mmol) in THF (5 mL) was then added. The resulting mixture was allowed to warm to r.t., and the reaction was stirred overnight. The mixture was then diluted with water (50 mL) and extracted with CH₂Cl₂ (3 × 25 mL). The combined organic layers were washed with water, dried over MgSO₄ and concentrated under reduced pressure. The crude residue was purified by chromatography (SiO₂, AcOEt / hexanes 1:4), affording 385 mg (38 %) of 1-azadiene **4a** and 321 mg (21 %) of the phosphorated cyclic enamine **5**.

Syn and anti ethyl 4-(*p*-nitrophenyl)-2-*p*-tolylimino-3-(*E*)-butenoate (4a): Yellow solid (syn / anti

= 40 / 60). M.p. 98–99 °C (Et₂O). ¹H NMR (300 MHz, CDCl₃, 30 °C): δ 8.19 and 8.12 (d, ³*J*_{HH} = 8.8 Hz, and d, ³*J*_{HH} = 8.7 Hz, 2 H),

7.61 and 7.41 (d, $^3J_{\text{HH}} = 8.8$ Hz, and d, $^3J_{\text{HH}} = 8.7$ Hz, 2 H), 7.47 and 7.02 (d, $^3J_{\text{HH}} = 16.2$ Hz and d $^3J_{\text{HH}} = 16.3$ Hz, 1H), 7.29 and 6.76 (d, $^3J_{\text{HH}} = 16.3$ Hz and d $^3J_{\text{HH}} = 16.2$ Hz, 1H), 7.17 (d, $^3J_{\text{HH}} = 8.1$ Hz, 2H), 6.74 (d, $^3J_{\text{HH}} = 8.1$ Hz, 2H), 4.43 and 4.09 (q, $^3J_{\text{HH}} = 7.1$ Hz, and q, $^3J_{\text{HH}} = 7.2$ Hz, 2 H), 2.33 and 2.28 (s, 3 H), 1.42 and 0.98 (t, $^3J_{\text{HH}} = 7.1$ Hz, and t, $^3J_{\text{HH}} = 7.2$ Hz, 3 H). ^{13}C NMR (75 MHz, CDCl_3 , 30 °C): δ 164.3 and 164.0, 159.5 and 157.4, 147.7, 146.5 and 145.0, 141.3 and 141.1, 139.0 and 137.9, 135.4 and 135.3, 129.4 and 129.1, 128.0 and 127.9, 123.8 and 123.7, 121.6 and 120.6, 120.2 and 119.4, 62.2 and 61.5, 20.5 and 20.4, 13.7 and 13.4. FTIR (KBr) ν_{max} (cm^{-1}): 1732, 1599. EIMS m/z (amu): 338 (M^+ , 20), 265 (100), 216 (92). % Elem. Anal. calcd. for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_4$: C 67.44, H 5.36, N 8.28. Found C 67.51, H 5.40, N 8.23.

4-(Diphenylphosphinoyl)-5-(*p*-nitrophenyl)-3-*p*-tolylamino-5*H*-furan-2-one 5. White solid. M.p.

151-152 °C (CH_2Cl_2 / hexanes). ^1H NMR (300 MHz, CDCl_3): δ 8.16 (d, $^3J_{\text{HH}} = 8.7$ Hz, 2 H), 8.04 (d, $^3J_{\text{HH}} = 8.7$ Hz, 2 H), 7.40–7.31 (m, 10 H), 7.15 (d, $^3J_{\text{HH}} = 7.9$ Hz, 2 H), 7.06 (d, $^3J_{\text{HH}} = 7.9$ Hz, 2 H), 6.84 (s, 1 H) 6.65 (d, $^3J_{\text{PH}} = 3.1$ Hz, 1 H), 2.09 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 166.9 (d, $^3J_{\text{PC}} = 17.5$), 148.1, 144.1, 141.1, 135.5, 134.4, 130.0, 127.9, 123.1–132.7 (m), 129.9 (d, $^1J_{\text{PC}} = 74.9$ Hz), 121.8, 117.3 107.1 (d, $^1J_{\text{PC}} = 110.3$ Hz), 81.7 (d, $^2J_{\text{PH}} = 3.1$ Hz), 21.9. ^{31}P NMR: 22.7. FTIR (KBr) ν_{max} (cm^{-1}): 3363, 1779, 1175. EIMS m/z (amu): 510 (M^+ , 30), 309 (100). % Elem. Anal. calcd. for $\text{C}_{29}\text{H}_{23}\text{N}_2\text{O}_5\text{P}$: C, 68.23; H, 4.54; N, 5.49. Found: C, 68.20; H, 4.57; N, 5.52

General procedure for the synthesis of 1-azadienes 4. To a solution of the corresponding azide **8** (5 mmol) in CH_2Cl_2 (25 mL) at 0 °C was added a 1M solution of trimethylphosphine in toluene (5 mL). The resulting solution was stirred 30 min. until N_2 evolution stopped, which indicates the completion of the reaction and phosphazene **9** formation, and the corresponding neat β,γ -unsaturated α -ketoester **10** (5 mmol) was then added. The reaction was stirred at r.t. for 30 min. and was then washed with water (3×40 mL), dried over MgSO_4 and concentrated under reduced pressure. 1-Azadienes **4d-i** were used

without any further purification in the following steps, and 1-azadienes **4a-c** were purified by crystallization from Et₂O.

Syn and anti ethyl 4-(*p*-nitrophenyl)-2-*p*-tolylimino-3-(*E*)-butenoate 4a. Synthesized according to the general procedure with *p*-tolylazide (0.67 g, 5 mmol) and ethyl (*E*)-4-*p*-nitrophenyl-2-oxo-3-butenate (1.25 g, 5 mmol), affording 1.52 g (90 %) of **4a** as a yellow solid (*syn* / *anti* = 41 / 59). Spectroscopic data are in agreement with literature values.¹

Syn and anti ethyl 4-(*p*-nitrophenyl)-2-*p*-methoxyphenylimino-3-(*E*)-butenoate 4c. Synthesized according to the general procedure with *p*-methoxyphenylazide (0.75 g, 5 mmol) and ethyl (*E*)-4-*p*-nitrophenyl-2-oxo-3-butenate (1.25 g, 5 mmol), affording 1.61 g (91 %) of **4c** as a yellow solid (*syn* / *anti* = 43 / 57). M.p. 111–112 °C (Et₂O). ¹H NMR (300 MHz, CDCl₃): δ 8.24 and 8.18 (d, ³*J*_{HH} = 9.0 Hz, and d, ³*J*_{HH} = 9.0 Hz, 2 H), 7.66 and 7.52 (d, ³*J*_{HH} = 9.0 Hz, and d, ³*J*_{HH} = 9.0 Hz, 2 H), 7.51 and 6.87 (d, ³*J*_{HH} = 16.2 Hz, and d, ³*J*_{HH} = 16.3 Hz, 1 H), 7.17–6.88 (m, 5 H), 4.48 and 4.21 (q, ³*J*_{HH} = 7.2 Hz, and q, ³*J*_{HH} = 7.2 Hz, 2 H), 3.84 and 3.81 (s, 3 H), 1.47 and 1.08 (t, ³*J*_{HH} = 7.2 Hz, and t, ³*J*_{HH} = 7.2 Hz, 3 H). ¹³C NMR (75 MHz, CDCl₃): δ 164.7 and 164.6, 158.6 and 158.0 (C=NO), 157.9 and 156.7, 148.0 and 147.9, 142.7 and 141.8, 141.6 and 141.3, 138.5 and 137.2, 130.1 and 122.5, 128.1 and 128.0, 124.1 and 124.0, 121.5 and 121.3, 114.3 and 114.1, 62.3 and 61.7, 55.4, 14.1 and 13.8. FTIR (KBr) ν_{max} (cm⁻¹): 1712, 1593. CIMS *m/z* (amu): 355 (M⁺+1, 100). % Elem. Anal. calcd. for C₁₈H₁₅N₃O₆: C, 64.40; H, 5.12; N, 7.91. Found: C, 64.37; H, 5.16; N, 7.94.

Syn and anti methyl 4-(*p*-tolyl)-2-*p*-tolylimino-but-3-enoate 4d. Synthesized according to the general procedure with *p*-tolylazide (0.67 g, 5 mmol) and methyl (*E*)-4-*p*-tolyl-2-oxo-3-butenate (1.02 g, 5 mmol), affording 1.30 g (89 %) of crude **4d** as an orange oil (*syn* / *anti* = 41 / 59). *R_f* (AcOEt): 0.98. ¹H NMR (300 MHz, CDCl₃): δ 7.42 and 7.25 (d, ³*J*_{HH} = 8.1 Hz, and d, ³*J*_{HH} = 8.1 Hz, 2 H), 7.40 and 7.18 (d, ³*J*_{HH} = 16.4 Hz, and d, ³*J*_{HH} = 16.2 Hz, 1 H), 7.21 and 7.15 (d, ³*J*_{HH} = 16.4

Hz, and d, $^3J_{\text{HH}} = 16.3$ Hz, 2 H), 7.12 (d, $^3J_{\text{HH}} = 8.1$ Hz, 2 H), 6.84 (d, $^3J_{\text{HH}} = 8.1$ Hz, 2 H), 7.03 and 6.68 (d, $^3J_{\text{HH}} = 16.4$ Hz, and d, $^3J_{\text{HH}} = 16.2$ Hz, 1 H), 3.99 and 3.65 (s, 3 H), 2.37 (s, 3 H), 2.33 and 2.32 (s, 3 H). ^{13}C NMR (75 MHz, CDCl_3): δ 164.3 and 164.0, 159.5 and 157.4, 146.5 and 145.5, 142.2 and 141.1, 140.3 and 140.1, 134.7 and 134.6, 132.6 and 132.5, 129.1 and 125.0, 119.6 and 119.5, 119.4 and 119.3, 127.8 and 127.6, 120.4 and 119.7, 52.8 and 51.8, 21.3, 20.9. FTIR (KBr) ν_{max} (cm^{-1}) 1732, 1597. CIMS m/z (amu): 294 ($\text{M}^+ + 1$, 100).

Syn and anti methyl 4-*p*-tolyl-2-*p*-nitrophenylimino-but-3-enoate 4e. Synthesized according to the

general procedure with *p*-nitrophenylazide (0.67 g, 5 mmol) and methyl (*E*)-4-*p*-tolyl-2-oxo-3-butenolate (0.82 g, 5 mmol), affording

1.39 g (82 %) of crude **4e** as an orange oil (syn / anti = 43 / 57). R_f

(AcOEt): 0.96. ^1H NMR (300 MHz, CDCl_3): δ 8.26 and 8.19 (d, $^3J_{\text{HH}} =$

8.7 Hz, and d, $^3J_{\text{HH}} = 8.7$ Hz, 2 H), 8.03 and 7.85 (d, $^3J_{\text{HH}} = 9.1$ Hz, and d, $^3J_{\text{HH}} = 16.3$ Hz, 1 H), 7.44

and 7.27 (d, $^3J_{\text{HH}} = 7.8$ Hz and $^3J_{\text{HH}} = 8.2$ Hz, 2 H), 7.21 and 7.18 (d, $^3J_{\text{HH}} = 8.2$ Hz and $^3J_{\text{HH}} = 7.8$ Hz,

2 H), 7.00 and 6.94 (d, $^3J_{\text{HH}} = 8.7$ Hz and $^3J_{\text{HH}} = 8.7$ Hz, 2 H), 6.60 and 6.43 (d, $^3J_{\text{HH}} = 9.1$ Hz, and d,

$^3J_{\text{HH}} = 16.3$ Hz, 1 H), 4.01 and 3.63 (s, 3 H), 2.38 and 2.34 (s, 3 H). ^{13}C NMR (75 MHz, CDCl_3): δ

164.0 and 163.1, 160.7 and 159.0, 155.5 and 154.2, 153.4 and 148.0, 144.7 and 143.0, 144.0 and

143.9, 140.8 and 140.5, 129.2, 127.6 and 127.5, 124.5 and 124.2, 119.6 and 119.3, 114.4 and 112.5,

52.5 and 51.6, 20.9 and 20.8. FTIR (KBr) ν_{max} (cm^{-1}) 1735, 1592. CIMS m/z (amu): 325 ($\text{M}^+ + 1$, 100).

Syn and anti ethyl 2-*p*-methoxyphenylimino-3-(*E*)-pentenoate 4f. Synthesized according to the

general procedure with *p*-methoxyphenylazide (0.75 g, 5 mmol) and ethyl (*E*)-

2-oxo-3-pentenoate (0.71 g, 5 mmol), affording 1.39 g (91 %) of crude **4f** as

an orange oil (syn / anti = 36 / 64). R_f (AcOEt): 0.95. ^1H NMR (300 MHz,

CDCl_3): δ 7.29 and 7.19 (d, $^3J_{\text{HH}} = 16.4$ Hz, and d, $^3J_{\text{HH}} = 16.2$ Hz, 1 H), 6.92–6.81 (m, 4 H, 4 CHar),

6.61 and 6.16 (d, $^3J_{\text{HH}} = 16.2$ Hz, and d, $^3J_{\text{HH}} = 16.4$ Hz, 1 H), 4.38 and 4.09 (q, $^3J_{\text{HH}} = 7.2$ Hz, and q,

$^3J_{\text{HH}} = 7.1$ Hz, 2 H), 3.82 and 3.78 (s, 3 H), 1.96 and 1.85 (d, $^3J_{\text{HH}} = 5.0$ Hz, and d, $^3J_{\text{HH}} = 5.0$ Hz, 3 H),

1.42 and 1.04 (t, $^3J_{\text{HH}} = 7.2$ Hz, and t, $^3J_{\text{HH}} = 7.1$ Hz, 3 H). ^{13}C NMR (75 MHz, CDCl_3): δ 166.2 and

166.5, 160.5 and 159.8, 157.1 and 157.0, 143.1 and 142.0, 142.2 and 140.7, 130.4 and 121.5, 122.0 and 119.8, 114.4 and 114.2, 62.2 and 61.5, 55.7, 19.4 and 19.1, 14.4 and 14.0. CIMS m/z (amu): 248 ($M^+ + 1$, 100).

Syn and anti ethyl 4-(2-furyl)-2-*p*-methoxyphenylimino-(*E*)-3-butenolate 4g. Synthesized

according to the general procedure with *p*-methoxyphenylazide (0.75 g, 5 mmol) and ethyl 4-(2-furyl)-2-oxo-3-(*E*)-butenoate (0.97 g, 5 mmol), affording 1.39 g (91 %) of crude **4g** as an orange oil (syn / anti = 44 / 66).

R_f (AcOEt): 0.95. ^1H NMR (300 MHz, CDCl_3): δ 7.66–7.28 (m, 4 H), 6.96–6.22 (m, 5 H), 4.45 and 4.12 (q, $^3J_{\text{HH}} = 7.2$ Hz, and q, $^3J_{\text{HH}} = 7.1$ Hz, 2 H), 3.82 and 3.77 (s, 3 H), 1.41 and 1.02 (t, $^3J_{\text{HH}} = 7.2$ Hz, and t, $^3J_{\text{HH}} = 7.1$ Hz, 3 H). ^{13}C NMR (75 MHz, CDCl_3): δ 166.8 and 165.0, 157.8 and 157.3, 152.0 and 151.7, 145.5 and 144.4, 144.5 and 141.9, 133.5, 128.2 and 123.8, 127.2 and 125.3, 122.2 and 121.4, 116.4 and 115.1, 114.1 and 114.0, 112.4 and 112.3, 62.1 and 61.4, 55.4, 14.2 and 14.1. CIMS m/z (amu): 300 ($M^+ + 1$, 100).

Syn and anti ethyl 4-ethoxycarbonyl-2-*p*-nitrophenylimino-3-(*E*)- butenoate 4h. Synthesized

according to the general procedure with *p*-nitrophenylazide (0.82 g, 5 mmol) and ethyl (*E*)-4-ethoxycarbonyl-2-oxo-3-butenolate (1.00 g, 5 mmol), affording 1.50 g (94 %) of crude **4h** as an orange oil (syn / anti =

42 / 68). R_f (AcOEt): 0.95. ^1H NMR (300 MHz, CDCl_3): δ 8.19 and 8.13 (d, $^3J_{\text{HH}} = 8.7$ Hz, and d, $^3J_{\text{HH}} = 8.9$ Hz, 2 H), 7.32 and 6.90 (d, $^3J_{\text{HH}} = 16.2$ Hz, and d, $^3J_{\text{HH}} = 16.2$ Hz, 1 H), 6.89 and 6.85 (d, $^3J_{\text{HH}} = 8.9$ Hz, and d, $^3J_{\text{HH}} = 8.7$ Hz, 2 H), 6.68 and 6.50 (d, $^3J_{\text{HH}} = 16.2$ Hz, and d, $^3J_{\text{HH}} = 16.2$ Hz, 1 H), 4.38 and 4.04 (q, $^3J_{\text{HH}} = 7.0$ Hz, and q, $^3J_{\text{HH}} = 7.0$ Hz, 2 H), 4.22 and 4.12 (q, $^3J_{\text{HH}} = 7.2$ Hz, and q, $^3J_{\text{HH}} = 7.2$ Hz, 2 H), 1.36 and 0.94 (t, $^3J_{\text{HH}} = 7.0$ Hz, and t, $^3J_{\text{HH}} = 7.0$ Hz, 3 H), 1.26 and 1.19 (t, $^3J_{\text{HH}} = 7.2$ Hz, and t, $^3J_{\text{HH}} = 7.2$ Hz, 3 H). ^{13}C NMR (75 MHz, CDCl_3): δ 165.0 and 164.8, 162.8 and 161.7, 159.3 and 157.3, 154.9 and 153.3, 145.2 and 144.9, 138.2 and 131.5, 132.9 and 129.4, 125.0 and 124.6,

119.6 and 119.2, 62.8 and 62.2, 61.4 and 61.3, 14.7 and 13.8, 14.6 and 14.0. CIMS m/z (amu): 321 ($M^+ + 1$, 100).

Syn and anti ethyl 4-ethoxycarbonyl-2-*p*-tolylimino-3-(*E*)-butenoate **4i** Synthesized according to

the general procedure with *p*-tolylazide (0.67 g, 5 mmol) and ethyl (*E*)-4-ethoxycarbonyl-2-oxo-3-butenate (1.00 g, 5 mmol), affording 1.36 g (94 %)

of crude **4i** as an orange oil (syn / anti = 40 / 60). R_f (AcOEt): 0.96. ^1H NMR (300 MHz, CDCl_3): δ 7.40 and 7.24 (d, $^3J_{\text{HH}} = 16.2$ Hz, and d, $^3J_{\text{HH}} = 16.3$ Hz, 1 H), 7.17 and 7.11 (d, $^3J_{\text{HH}} = 8.4$ Hz, and d, $^3J_{\text{HH}} = 8.4$ Hz, 2 H), 6.82 and 6.79 (d, $^3J_{\text{HH}} = 8.4$ Hz, and d, $^3J_{\text{HH}} = 8.4$ Hz, 2 H), 6.71 and 6.44 (d, $^3J_{\text{HH}} = 16.2$ Hz, and d, $^3J_{\text{HH}} = 16.3$ Hz, 1 H), 4.43 and 4.11 (q, $^3J_{\text{HH}} = 7.0$ Hz, and q, $^3J_{\text{HH}} = 7.0$ Hz, 2 H), 4.27 and 4.21 (q, $^3J_{\text{HH}} = 7.2$ Hz, and q, $^3J_{\text{HH}} = 7.2$ Hz, 2 H), 2.35 and 2.32 (s, 3 H), 1.48 and 1.03 (t, $^3J_{\text{HH}} = 7.0$ Hz, and t, $^3J_{\text{HH}} = 7.0$ Hz, 3 H), 1.33 and 1.27 (t, $^3J_{\text{HH}} = 7.2$ Hz, and t, $^3J_{\text{HH}} = 7.2$ Hz, 3 H). ^{13}C NMR (75 MHz, CDCl_3): δ 165.4 and 164.9, 163.5 and 163.2, 157.8 and 155.6, 146.5 and 144.9, 139.6 and 130.0, 135.8 and 135.7, 130.5 and 129.7, 129.3 and 129.1, 120.2 and 119.2, 61.9 and 61.3, 60.9 and 60.7, 20.5 and 20.4, 13.7 and 13.3, 13.6 and 13.5. CIMS m/z (amu): 290 ($M^+ + 1$, 100).

Syn and anti ethyl 4-ethoxycarbonyl-2-*p*-methoxyphenylimino-(*E*)-3-butenate **4j**. Synthesized

according to the general procedure with *p*-methoxyphenylazide (0.75 g, 5 mmol) and ethyl (*E*)-4-ethoxycarbonyl-2-oxo-3-butenate (1.00 g, 5 mmol), affording 1.45 g (95 %) of crude **4j** as an orange oil (syn / anti = 41

/ 59). R_f (AcOEt): 0.96. ^1H NMR (300 MHz, CDCl_3): δ 7.33 and 7.14 (d, $^3J_{\text{HH}} = 16.3$ Hz, and d, $^3J_{\text{HH}} = 16.2$ Hz, 1 H), 6.88–6.77 (m, 4 H, 4 CHar), 6.66 and 6.34 (d, $^3J_{\text{HH}} = 16.3$ Hz, and d, $^3J_{\text{HH}} = 16.2$ Hz, 1 H), 4.36 and 4.07 (q, $^3J_{\text{HH}} = 7.0$ Hz, and q, $^3J_{\text{HH}} = 7.0$ Hz, 2 H), 4.17 and 4.14 (q, $^3J_{\text{HH}} = 7.2$ Hz, and q, $^3J_{\text{HH}} = 7.2$ Hz, 2 H), 3.75 and 3.73 (s, 3 H), 1.35 and 1.02 (t, $^3J_{\text{HH}} = 7.0$ Hz, and t, $^3J_{\text{HH}} = 7.0$ Hz, 3 H), 1.25 and 1.21 (t, $^3J_{\text{HH}} = 7.2$ Hz, and t, $^3J_{\text{HH}} = 7.2$ Hz, 3 H). ^{13}C NMR (75 MHz, CDCl_3): δ 165.8 and 165.3, 163.9 and 163.8, 158.5 and 158.2, 157.1 and 154.8, 142.2 and 140.6, 140.1 and 129.9,

131.1 and 128.8, 122.8 and 121.5, 114.1 and 113.9, 62.1 and 61.5, 60.9 and 60.8, 55.2, 13.9 and 13.5, 13.8 and 13.6. CIMS m/z (amu): 306 ($M^+ + 1$, 100).

Procedure for the selective reduction of 1-azadienes **1 with NaBH_4 . Synthesis of α -dehydroaminoacids **11**:** To a suspension of NaBH_4 (76 mg, 2 mmol) in THF (3 mL) at -78°C was added a solution of 1-azadiene **4** (1 mmol) in THF (2 mL). The reaction was stirred at -78°C for 12 h and was then quenched with a sat. aq. solution of NH_4Cl (20 mL). The mixture was warmed to r.t, extracted with CH_2Cl_2 , (3×15 mL), dried over MgSO_4 and concentrated under reduced pressure. The crude residue was purified by chromatography (SiO_2 , AcOEt / hexanes 1:3).

Ethyl 4-ethoxycarbonyl-2-*p*-nitrophenylamino-(*Z*)-2-butenate **11b** Synthesized according to the general procedure with crude ethyl 4-ethoxycarbonyl-2-*p*-nitrophenylimino-(*E*)-3-butenate **4h** (0.320 mg, 1 mmol), affording 0.251 mg (75 %) of **11b** as a pale yellow oil. R_f (AcOEt): 0.85. ^1H NMR (300 MHz, CDCl_3): δ 8.12 (d, $^3J_{\text{HH}} = 9.0$ Hz, 2 H), 7.32 (t, $^3J_{\text{HH}} = 7.3$ Hz, 1 H), 6.63 (d, $^3J_{\text{HH}} = 9.0$ Hz, 2 H), 6.24 (s, 1 H), 4.26 (q, $^3J_{\text{HH}} = 7.2$ Hz, 2 H), 4.17 (q, $^3J_{\text{HH}} = 7.2$ Hz, 2 H), 3.13 (d, $^3J_{\text{HH}} = 7.3$ Hz, 2 H), 1.30 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3 H), 1.26 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3 H). ^{13}C NMR (75 MHz, CDCl_3): δ 170.3, 164.6, 150.0, 140.5, 130.9, 126.6, 126.1, 114.2, 62.2, 61.7, 34.1, 14.4, 14.2. FTIR (film) ν_{max} (cm^{-1}): 3363, 1732. CIMS m/z (amu): 323 ($M^+ + 1$, 100). % Elem. anal. calcd. for $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}_6$: C, 55.90; H, 5.63; N, 8.69. Found: C, 55.85; H, 5.60; N, 8.73.

Ethyl 4-ethoxycarbonyl-2-*p*-tolylamino-2-(*Z*)-butenoate **11c** Synthesized according to the general procedure with crude ethyl 4-ethoxycarbonyl-2-*p*-tolylimino-(*E*)-3-butenate **4i** (0.289 mg, 1 mmol), affording 0.23 g (79 %) of **11c** as a pale yellow oil. R_f (AcOEt): 0.88. ^1H NMR (300 MHz, CDCl_3): δ 7.01 (d, $^3J_{\text{HH}} = 7.2$ Hz, 2 H), 6.60 (d, $^3J_{\text{HH}} = 7.2$ Hz, 2 H), 6.49 (t, $^3J_{\text{HH}} = 7.2$ Hz, 1 H), 5.75 (s, 1 H), 4.24 (q, $^3J_{\text{HH}} = 7.2$ Hz, 2 H), 4.13 (q, $^3J_{\text{HH}} = 7.2$ Hz, 2 H), 3.03 (d, $^3J_{\text{HH}} = 7.2$ Hz, 2 H), 2.25 (s, 3 H), 1.29 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3 H), 1.23 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3 H). ^{13}C NMR (75 MHz, CDCl_3): δ 170.9, 165.5, 154.1 (C) 140.8, 129.1,

129.3, 126.5, 117.1, 62.2, 61.7, 34.1, 20.8, 14.1, 13.9. FTIR (film) $\nu_{\max}$ (cm^{-1}): 3360, 1740. CIMS m/z (amu): 292 ($M^+ + 1$, 100). % Elem. anal. calcd. for $\text{C}_{16}\text{H}_{21}\text{NO}_4$: C 65.96, H 7.27, N 4.81. Found: C 66.02, H 7.31, N 4.78.

Ethyl 2-(*p*-methoxyphenylamino)-pent-2-enoate **11d:** Synthesized according to the general procedure with ethyl 2-*p*-methoxyphenylimino-3-(*E*)-pentenoate **4f** (0.247 mg, 1 mmol), affording 0.175 mg (71 %) of **11d** as a pale yellow oil. R_f (AcOEt): 0.89. ^1H NMR (300 MHz, CDCl_3): δ 6.72 (d, $^3J_{\text{HH}} = 7.1$ Hz, 2 H), 6.70 (t, $^3J_{\text{HH}} = 7.2$ Hz, 1 H), 6.50 (d, $^3J_{\text{HH}} = 7.1$ Hz, 2 H), 4.26 (q, $^3J_{\text{HH}} = 7.2$ Hz, 2 H), 4.18 (s, 1 H), 4.13 (q, $^3J_{\text{HH}} = 7.2$ Hz, 2 H, CH_2O), 3.70 (s, 3H), 1.88 (m, 2 H), 1.27 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3 H, CH_3), 1.18 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3 H, CH_3). ^{13}C NMR (75 MHz, CDCl_3): δ 165.3, 151.8, 141.6, 127.8, 115.0, 114.4, 60.5, 55.3, 19.0, 18.6, 13.9. FTIR (film) $\nu_{\max}$ (cm^{-1}), 3360, 1740. CIMS m/z (amu): 250 ($M^+ + 1$, 100). Elem. anal. calcd. for $\text{C}_{14}\text{H}_{19}\text{NO}_3$: C, 67.45; H, 7.68; N, 5.62. Found: C, 67.41; H, 7.71; N, 5.60.

Ethyl 4-furan-2-yl-2-(4-methoxy-phenylamino)-but-2-enoate **11e:** Synthesized according to the general procedure with ethyl 4-furan-2-yl-2-(4-methoxy-phenylimino)-but-3-enoate **4g** (0.300 mg, 1 mmol), affording 0.233 mg (64 %) of **11e** as a pale yellow oil. R_f (AcOEt): 0.87. ^1H NMR (300 MHz, CDCl_3): δ 7.31 (d, $^3J_{\text{HH}} = 1.8$ Hz, 1 H), 7.26 (d, $^3J_{\text{HH}} = 9.1$ Hz, 2 H), 6.84 (d, $^3J_{\text{HH}} = 7.2$ Hz, 2 H, 2CH ar), 6.26 (dd, $^3J_{\text{HH}} = 1.8$ Hz, $^3J_{\text{HH}} = 3.1$ Hz, 1 H), 6.20 (t, $^3J_{\text{HH}} = 7.2$ Hz, 1 H), 6.15 (d, $^3J_{\text{HH}} = 3.1$ Hz, 1 H), 5.99 (s, 1 H), 4.26 (q, $^3J_{\text{HH}} = 7.2$ Hz, 2 H), 3.79 (s, 3 H), 3.51 (d, $^3J_{\text{HH}} = 7.2$ Hz, 2 H), 1.30 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3 H). ^{13}C NMR (75 MHz, CDCl_3): δ 165.6, 154.5, 151.6, 147.4, 141.2, 140.0, 123.7, 117.6, 117.2, 109.1, 106.3, 61.7, 55.6, 34.5, 14.2. FTIR (film) $\nu_{\max}$ (cm^{-1}), 3363, 1737. CIMS m/z (amu): 302 ($M^+ + 1$, 100). Elem. anal. calcd. for $\text{C}_{17}\text{H}_{19}\text{NO}_4$: C, 67.76; H, 6.36; N, 4.65. Found: C, 67.81; H, 6.33; N, 4.61.

Procedure for the hydrolysis of α -dehydroamino esters **11.** To a solution of α -dehydroamino ester **11** (0.5 mmol) in THF (1 mL) was added a 3 M aqueous solution of HCl (1 mL) and the resulting

mixture was refluxed overnight. The reaction was cooled to r.t and neutralized with a saturated aqueous solution of NaHCO₃ (10 mL) and extracted with CH₂Cl₂ (2 × 15 mL) which was dried over MgSO₄ and concentrated under reduced pressure. The crude residue was purified by chromatography (SiO₂, AcOEt / hexanes 1:3).

Diethyl 2-oxo-pentanediate 12b. Synthesized according to the general procedure with ethyl 4-ethoxycarbonyl-2-*p*-tolylamino-2-(*Z*)-butenoate **11b** (146 mg, 0.5 mmol), affording 86 mg (85 %) of **12b** as a colorless oil. Spectroscopic data are in agreement with literature values.⁴

Procedure for the selective 1,2 reduction of 1-azadienes 4 with NaBH₄ in the presence of TFA.

Synthesis of vinylglycines 13: NaBH₄ (76 mg, 2 mmol) was slowly added to a solution of the corresponding 1-azadiene **4** (1 mmol) and TFA (0.5 mL) in MeCN (3 mL) at 0 °C. The resulting mixture was stirred at 0 °C for 3 h. and was then quenched with an aqueous saturated solution of NaHCO₃ (15 mL), extracted with CH₂Cl₂ (3 × 20 mL), dried over MgSO₄ and concentrated under reduced pressure. The crude residue was purified by crystallization from MeOH.

Ethyl 4-(4-nitro-phenyl)-2-*p*-tolylamino-but-3-enoate 13b. Synthesized according to the general

procedure with ethyl 4-*p*-nitrophenyl-2-*p*-tolylimino-(*E*)-3-butenate **4a** (338 mg, 1 mmol), affording 289 mg (85 %) of **13b** as

a yellow solid. M.p. 109–110 °C (Et₂O). ¹H NMR (300 MHz, CDCl₃): δ 8.17 (d, ³*J*_{HH} = 8.8 Hz, 2 H), 7.50 (d, ³*J*_{HH} = 8.8 Hz, 2 H),

7.02 (d, ³*J*_{HH} = 8.3 Hz, 2 H), 6.86 (d, ³*J*_{HH} = 15.9 Hz, 1 H), 6.59 (d, ³*J*_{HH} = 8.3 Hz, 2 H), 6.53 (dd, ³*J*_{HH} = 15.9 Hz, ³*J*_{HH} = 5.2 Hz, 1 H), 4.75 (d, ³*J*_{HH} = 5.2 Hz, 1 H), 4.62 (s, 1 H), 4.36 – 4.24 (m, 2 H, CH₂O diastereotopic), 2.26 (s, 3 H), 1.33 (t, ³*J*_{HH} = 7.0 Hz, 3 H). ¹³C NMR (75 MHz, CDCl₃): δ 171.0, 147.0, 143.8, 142.6, 130.3, 130.2, 129.8, 127.8, 127.2, 123.9, 113.7, 62.0, 59.1, 20.3, 14.1. FTIR (KBr) ν_{max} (cm⁻¹): 3342, 1736. CIMS m/z (amu): 340 (M⁺, 22), 267 (100). Elem. anal. calcd. for C₁₉H₂₀N₂O₄: C, 67.05; H, 5.92; N, 8.23. Found: C, 67.10; H, 5.89; N, 8.24.

Ethyl (*E*)-2-*p*-methoxyphenylamino-4-*p*-nitrophenyl-3-butenolate **13c.** Synthesized according to

the general procedure with ethyl 2-*p*-methoxyphenylimino-4-*p*-nitrophenyl-(*E*)-3-butenolate **4c** (354 mg, 1 mmol), affording 294

mg (82 %) of **13c** as a yellow solid. M.p. 119–120 °C (Et₂O).

¹H NMR (300 MHz, CDCl₃): δ 8.17 (d, ³*J*_{HH} = 8.9 Hz, 2 H), 7.57 (d, ³*J*_{HH} = 8.9 Hz, 2 H), 6.86 (d, ³*J*_{HH} = 15.9 Hz, 1 H), 6.63 (d, ³*J*_{HH} = 9.0 Hz, 2 H), 6.79 (d, ³*J*_{HH} = 9.0 Hz, 2 H), 6.53 (dd, ³*J*_{HH} = 15.9 Hz, ³*J*_{HH} = 5.3 Hz, 1 H), 4.69 (d, ³*J*_{HH} = 5.3 Hz, 1 H), 4.33 (s, 1 H), 4.37 – 4.20 (m, 2 H), 3.74 (s, 3 H), 1.32 (t, ³*J*_{HH} = 7.2 Hz, 3 H). ¹³C NMR (75 MHz, CDCl₃): δ 171.0, 152.6, 146.8, 142.5, 140.1, 130.3, 130.2, 127.0, 123.7, 114.8, 114.7, 61.9, 59.5, 55.4, 14.0. FTIR (KBr) ν_{max} (cm⁻¹): 3350, 1732. EIMS *m/z* (amu): 356 (M⁺, 45), 283 (100). Elem. anal. calcd. for C₁₉H₂₀N₂O₅: C, 64.04; H, 5.66; N, 7.86. Found: C, 63.97; H, 5.69; N, 7.81.

Methyl 4-*p*-tolyl-2-*p*-tolylamino-but-3-enoate **13d.** Synthesized according to the general procedure

with ethyl 4-*p*-tolyl-2-*p*-tolylimino-(*E*)-3-butenolate **4b** (338 mg, 1 mmol), affording 293mg (86 %) of **13c** as a yellow solid. M.p. 100–

101 °C (Et₂O). ¹H NMR (300 MHz, CDCl₃): δ 7.27 (d, ³*J*_{HH} = 7.8 Hz, 2

H), 7.11 (d, ³*J*_{HH} = 7.9 Hz, 2 H), 6.98 (d, ³*J*_{HH} = 7.9 Hz, 2 H), 6.74 (d,

³*J*_{HH} = 15.9 Hz, 1 H), 6.59 (d, ³*J*_{HH} = 7.8 Hz, 2 H), 6.22 (dd, ³*J*_{HH} = 15.9 Hz, ³*J*_{HH} = 6.0 Hz, 1 H), 4.70

(d, ³*J*_{HH} = 6.0 Hz, 1 H), 4.66 (s, 1 H), 3.79 (m, 3 H), 2.33 (s, 3 H), 2.24 (s, 3 H). ¹³C NMR (75 MHz,

CDCl₃): δ 172.4, 144.0, 137.9, 142.6, 133.3, 132.8, 129.7, 129.2, 127.5, 124.0, 113.7, 59.2, 52.6, 21.2,

20.3. FTIR (KBr) ν_{max} (cm⁻¹): 3339, 1733. CIMS *m/z* (amu): 295 (M⁺, 21), 236 (100). Elem. anal.

calcd. for C₁₉H₂₁NO₂: C, 77.26; H, 7.17; N, 4.74. Found: C, 77.22; H, 7.20; N, 4.72.

4. (a) Drioli, S.; Nitti, P.; Pitacco, G.; Tossut L.; Valentin, E.; *Tetrahedron: Asymmetry* **1999**, *10*, 2713–2728. (b) Cappon, J.

Ethyl 2-(*p*-methoxy-phenylamino)-pent-3-enoate 13e. Synthesized according to the general

procedure with 2-*p*-methoxyphenylimino-3-(*E*)-pentenoate **4f** (247 mg, 1 mmol), affording 227mg (91 %) of **13e** as a yellow solid. M.p. 84–86 °C

(Et₂O). ¹H NMR (300 MHz, CDCl₃): δ 7.10 (d, ³*J*_{HH} = 8.8 Hz, 2 H), 6.91 (d, ³*J*_{HH} = 15.8 Hz, 1 H), 6.79 (d, ³*J*_{HH} = 8.8 Hz, 2 H), 6.63 (dd, ³*J*_{HH} = 15.8 Hz, ³*J*_{HH} = 5.3 Hz, 1 H), 4.35 – 4.15 (m, 2 H), 4.03 (d, ³*J*_{HH} = 5.3 Hz, 1 H), 4.01 (s, 1 H), 3.77 (s, 3 H), 1.55 (d, ²*J*_{HH} = 12.9 Hz, 3H), 1.30 (t, ³*J*_{HH} = 7.2 Hz, 3 H). ¹³C NMR (75 MHz, CDCl₃): δ 171.1, 149.5, 140.1, 131.8, 124.1, 123.9, 114.4, 61.0, 59.4, 55.3, 16.7, 13.7. FTIR (KBr) ν_{max} (cm⁻¹): 3331, 1737. CIMS *m/z* (amu): 250 (M⁺, 21), 276 (100). Elem. anal. calcd. for C₁₄H₁₉NO₃: C, 67.45; H, 7.68; N, 5.62. Found: C, 67.41; H, 7.71; N, 5.58.

Procedure for the the total reduction of 1-azadienes **4**. Synthesis of α-aminoesters **14**. Procedure

A: catalytic hydrogenation of 1-azadienes **4** or vinylglycines **13**. A solution of 1-azadiene **4** or vinylglycine **13** (1 mmol) in EtOH (5 mL) with Pd-C (10 %) (53 mg, 0.05 mmol) was stirred overnight under H₂ atmosphere at 80 psi. The resulting mixture was filtered through celite and concentrated under reduced pressure. The crude residue was purified by chromatography (SiO₂, AcOEt / hexanes 1:3).

Procedure B: Reduction of 1-azadienes **4** or α-dehydroamino esters **11** with NaBH₄. Over a solution of β,γ-unsaturated 1-azadiene **4** or α-dehydroamino ester **11** (1 mmol) in THF at -30 °C was added NaBH₄ (2 mmol). The resulting mixture was stirred at -30 °C for 3 h., quenched with a saturated aqueous solution of NH₄Cl and extracted with CH₂Cl₂, which was dried over MgSO₄. The crude residue was purified by chromatography (SiO₂, AcOEt / hexanes 1:3).

Diethyl 2-*p*-methoxyphenylaminopentanediate 14b. Synthesized according to the general

procedure A with crude 4-ethoxycarbonyl-2-*p*-methoxyphenylimino-(*E*)-3-butenate **4j** (305 mg, 1 mmol), affording 274 mg (87 %) of **14b** as a

colorless oil. Synthesized according to the general procedure B with crude 4-ethoxycarbonyl-2-*p*-methoxyphenylimino-(*E*)-3-butenate **4j** (305 mg, 1 mmol), affording 252 mg

(81 %) of **14b** as a colorless oil. R_f (AcOEt): 0.90. ^1H NMR (300 MHz, CDCl_3): δ = 6.76 (d, $^3J_{\text{HH}}$ = 8.2 Hz, 2 H), 6.60 (d, $^3J_{\text{HH}}$ = 8.2 Hz, 2 H), 4.20–3.97 (m, 5 H), 3.89 (s, 1 H), 3.73 (s, 3 H), 2.48 (t, $^3J_{\text{HH}}$ = 7.2 Hz, 2 H), 2.04–2.17 (m, 2 H), 1.25 (t, $^3J_{\text{HH}}$ = 7.2 Hz, 3 H), 1.23 (t, $^3J_{\text{HH}}$ = 7.2 Hz, 3 H). ^{13}C NMR (75 MHz, CDCl_3): δ 173.1, 172.8, 152.6, 140.7, 115.1, 114.7, 61.0, 60.4, 57.1, 55.5, 30.3, 27.9, 14.0 (2 CH_3). FTIR (film) ν_{max} (cm^{-1}): 3369, 1727. EIMS m/z (amu): 309 (M^+ , 22), 236 (100). Elem. anal. calcd. for $\text{C}_{16}\text{H}_{23}\text{NO}_5$: C, 62.12; H, 7.49; N, 4.53; % found: C, 62.07; H, 7.53; N, 4.49.

Ethyl 2-*p*-methoxyphenylamino-4-*p*-nitrophenylbutanoate 14c. Synthesized according to the

general procedure A with ethyl 2-*p*-methoxyphenylimino-4-*p*-nitrophenyl-(*E*)-3-butenate **1c** (354 mg, 1 mmol), affording 0.32 g

(90 %) of **14c** as a pale yellow oil. Synthesized according to the general procedure A with ethyl (*E*)-2-*p*-methoxyphenylamino-4-*p*-

nitrophenyl-3-butenate **13c** (356 mg, 1 mmol), affording 333 mg (92 %) of **14c** as a pale yellow oil. R_f (AcOEt): 0.85. ^1H NMR (300 MHz, CDCl_3): δ 7.01 (d, $^3J_{\text{HH}}$ = 8.1 Hz, 2 H), 6.78 (d, $^3J_{\text{HH}}$ = 8.7 Hz, 2 H), 6.65 (d, $^3J_{\text{HH}}$ = 8.1 Hz, 2 H), 6.59 (d, $^3J_{\text{HH}}$ = 8.7 Hz, 2 H), 4.17 (q, $^3J_{\text{HH}}$ = 7.0 Hz, 2 H), 3.99 (t, $^3J_{\text{HH}}$ = 6.1 Hz, 1 H), 3.76 (s, 3 H), 3.62 (s, 1 H), 2.69 (t, $^3J_{\text{HH}}$ = 7.7 Hz, 2 H), 2.17–1.93 (m, 2 H), 1.26 (t, $^3J_{\text{HH}}$ = 7.2 Hz, 3 H). ^{13}C NMR (75 MHz, CDCl_3): δ 174.8, 152.9, 144.8, 141.3, 131.2, 129.6,), 115.6, 115.5, 115.1, 61.2, 57.5, 56.0, 35.4, 31.3, 14.5. FTIR (film) ν_{max} (cm^{-1}) 3356, 1735. EIMS m/z = 358 (M^+ , 40), 285 (100). Elem. anal. calcd. for $\text{C}_{16}\text{H}_{23}\text{NO}_4$: C, 63.67; H, 6.19; N, 7.82. Found: C, 63.72; H, 6.22; N, 7.79.

Ethyl 2-*p*-methoxyphenylaminopentanoate 14d. Synthesized according to the general procedure A

with crude ethyl 2-*p*-methoxyphenylimino-(*E*)-3-pentenoate **4f** (247 mg, 1 mmol), affording 224 g (88 %) of **14d** as a colorless oil. R_f (AcOEt): 0.97.

^1H NMR (300 MHz, CDCl_3): δ 6.78 (d, $^3J_{\text{HH}}$ = 8.8 Hz, 2 H), 6.62 (d, $^3J_{\text{HH}}$ = 8.8 Hz, 2 H), 4.18 (q, $^3J_{\text{HH}}$ = 7.1 Hz, 2 H), 3.99 (t, $^3J_{\text{HH}}$ = 6.6 Hz, 1 H), 3.88 (s, 1 H), 3.76 (s, 3 H), 1.83–1.71 (m, 2 H), 1.48 (m, 2 H), 1.25 (t, $^3J_{\text{HH}}$ = 7.1 Hz, 3 H), 0.98 (t, $^3J_{\text{HH}}$ = 7.3 Hz, 3 H). ^{13}C NMR (75 MHz, CDCl_3): δ 174.6, 152.7, 141.2, 115.1, 114.9, 60.8, 56.7, 55.7, 35.4, 18.9, 14.2, 13.8. FTIR (film)

$\nu_{\max}$ (cm⁻¹) 3373, 1739. EIMS m/z (amu): 251 (M^+ , 27), 178 (100). Elem. anal. calcd. for C₁₄H₂₁NO₃: % C, 66.91; H, 8.42; N, 5.57. Found: C 66.86; H 8.39; N 5.60.

Ethyl 4-(2-furyl)-2-*p*-methoxyphenylaminobutanoate **14e.** Synthesized according to the general

procedure A with crude ethyl 4-(2-furyl)-2-*p*-methoxyphenylimino-(*E*)-3-butenate **4g** (299 mg, 1 mmol), affording 220 mg (82 %) of **14e** as a pale yellow oil. R_f (AcOEt): 0.96. ¹H NMR (300 MHz, CDCl₃): δ 7.34 (d, ³ J_{HH} = 2.0 Hz, 1 H), 6.74 (d, ³ J_{HH} = 7.1 Hz, 2 H), 6.60 (d, ³ J_{HH} = 7.1 Hz, 2 H),

6.42 (d, ³ J_{HH} = 3.5 Hz, 1 H), 6.34 (dd, ³ J_{HH} = 2.0 Hz, ³ J_{HH} = 2.0 Hz, 1 H), 4.17 (q, ³ J_{HH} = 7.1 Hz, 2 H), 3.88 (t, ³ J_{HH} = 6.5 Hz, 1 H), 3.89 (s, 1 H), 3.73 (s, 3 H), 2.61 (t, ³ J_{HH} = 7.2 Hz, 2 H), 2.06–2.00 (m, 2 H), 1.25 (t, ³ J_{HH} = 7.1 Hz, 3 H). ¹³C NMR (75 MHz, CDCl₃): δ 174.4, 154.8, 152.6, 141.6, 140.4, 115.0, 114.6, 108.4, 107.3, 60.9, 57.9, 55.7 (CNH), 31.3, 25.6, 14.1. FTIR (film) $\nu_{\max}$ = 3374, 1741. EIMS m/z = 303 (M^+ , 21), 230 (100). Elem. anal. calcd. for C₁₇H₂₁NO₄: C, 67.31; H, 6.98; N, 4.62.

Procedure for the synthesis of diethyl glutamate **16.** To a solution of CAN (mg, 1.5 mmol) in

water (2 mL) was slowly added α -aminoester **14b** (155 mg, 0.5 mmol), in MeCN (2 mL) at 0 °C. The mixture was stirred for 1 h, and Na₂CO₃ was added until pH became 7. The mixture was filtered through celite, and the filtrate was extracted with CH₂Cl₂ (3 $\times$ 20 mL) which was dried over MgSO₄ and concentrated under reduced pressure. The crude residue was purified by chromatography (SiO₂, AcOEt / hexanes 5:1) affording 76 mg (71 %) of **16** as a colorless oil. Spectroscopic data are in agreement with literature values.⁵

⁵ Ikota, N.; Achiwa, K.; Yamada, S. *Chem. & Pharm. Bull.* **1983**, *31*, 887–894.