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CONSECUTIVE THREE-COMPONENT SYNTHESIS OF FILM LUMINESCENT INDOLONE MEROCYANINES WITH L-AMINO ACID ESTER DONORS

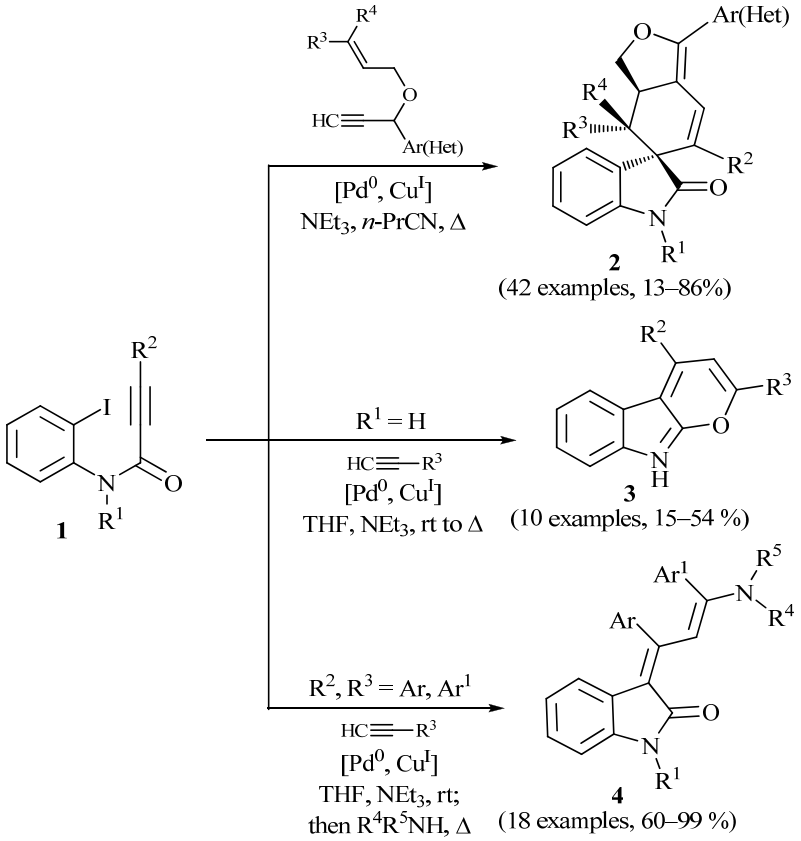
Prop-2-enylidene indolones substituted with L-amino acid esters are obtained in good to excellent yields in a consecutive three-component cyclocarbopalladation, Sonogashira coupling, and Michael addition sequence. While primary L-amino acid esters furnish a mixture of *E*,*E*- and *E*,*Z*-configurated diastereomers, L-proline methyl ester selectively and exclusively furnishes the *E*,*E*-isomer. As already discovered for other 3-aminoprop-2-enylidene indolones, the dropcasted films of all representatives display pronounced aggregation-induced orange-red fluorescence with large Stokes shifts, while all chromophores are nonemissive in solution.

Keywords: alkynes, amino acids, indolones, computations, cyclocarbopalladation, fluorescence, insertion, multicomponent reactions, Sonogashira coupling.

Functional π-electron systems [1], i. e. chromophores, fluorophores, and electrophores are key constituents in molecule-based electronics [2], molecular photonics [3], and biophysical analytics [4–6]. Therefore, their efficient preparation has remained an ongoing challenge for synthetic chemistry. Although multicomponent processes [7–18] and domino reactions [19–22] have significantly stimulated pharmaceutical lead discovery and development the concept of diversity-oriented synthesis [23–28] is still quite novel with respect to functional chromophores [29–31]. Transition metal-catalyzed processes have considerably enriched the construction of π-electron frameworks with extended conjugation. In addition, consecutive multicomponent syntheses of heterocycles based upon transition metal catalysis are particularly advantageous due to an excellent compatibility with numerous polar functionalities and mild reaction conditions [32–34].

With the Pd/Cu-catalyzed generation of alkynones and alkenones, based upon Sonogashira alkynylation, we have achieved a major breakthrough in the multicomponent syntheses of many classes of heterocycles [35–39]. In the past decade, we have developed a multicomponent methodology for the synthesis of chromophores [40, 41] and fluorophores [42–50]. Based upon a domino insertion–coupling sequence of alkynoyl *ortho*-iodo anilides **1** and alkynes, a straightforward access to indolone-based frameworks was disclosed leading to indolones **2** with conformationally rigidified, highly fluorescent butadiene units in a spirocyclic corset [51–53], protochromic pyranoindole fluorophores **3** [54], and solid-state luminescent push–pull chromophores **4** [55] with indolone as acceptor moiety.

In particular, the latter class of push–pull chromophores **4** is highly interesting since it represents a multicomponent approach to functional fluorophores. Most peculiar is the solid-state-only luminescence displaying strongly redshifted sharp emission bands, a similar behavior has also been observed for structurally related merocyanines [56]. Therefore, we became interested in expanding the scope of the three-component insertion – Sonogashira alkynylation – amine addition sequence of the push–pull chromophores **4** to bioorganic amino moieties such as amino acid

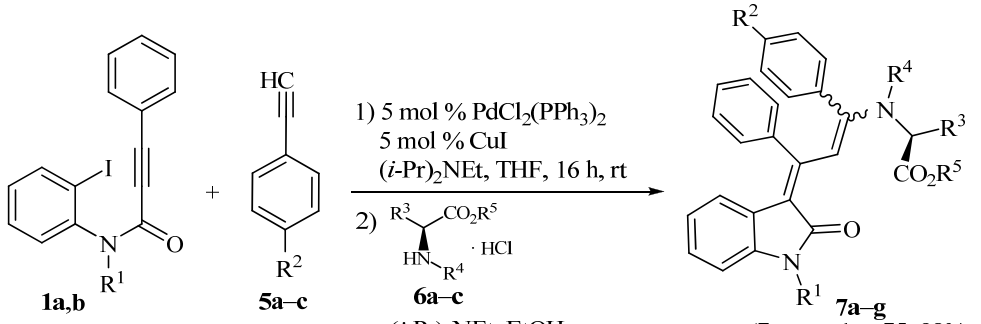


derivatives. Here, we report the synthesis of selected indolone merocyanines with L-amino acid ester donors, computationally based mechanistic considerations on the chromogenic amine addition, and the photophysical properties.

After the coupling between alkynoyl *ortho*-iodo anilides **1a**,**b** and terminal arylalkynes **5a**–**c** at room temperature under Sonogashira conditions forming ynylidene indolones as intermediates (not isolated, the reaction was monitored by TLC to ensure complete conversion), the latter were reacted with ethanolic solutions of the amino acid ester hydrochlorides **6a**–**c** at reflux temperature to give 3-amino acid ester-substituted prop-2-enylidene indolones **7a**–**g** in good to excellent yields as orange red solids.

The structures of the 3-amino acid ester-substituted prop-2-enylidene indolones **7a**–**g** were assigned by spectroscopic characterization and combustion analysis, and later corroborated by X-ray crystal structure analysis for compound **7g** (Fig. 1).

In contrary to the reaction with secondary amines, where the *E*,*E*-configured butadiene chromophores are formed with excellent stereoselectivity, primary amino acid esters give rise to the formation of a mixture of *E*,*E*- and *E*,*Z*-configured products **7a**–**e** in diastereomeric ratios ranging from 50:50 to 70:30 as indicated by the appearance of a second set of most signals in the ^{1}H and ^{13}C NMR spectra. The optical rotations of compounds **7a**–**e** are found between 7 and 13°. Again, the cyclic, secondary amine L-proline methyl ester gives rise to the exclusive, stereoselective formation of the *E*,*E*-configured butadiene chromophores **7f**,**g**, as indicated by the appearance of a single set of signals in the NMR spectra and as unambiguously proven by the X-ray structure analysis of compound **7g** (Fig. 1). In addition large optical rotations of 345 and 379° for compounds **7f** and **7g**, respectively, can be measured.



1a,b **5a–c** **6a–c** **7a–g** (7 examples, 75–98%; *dr* 50:50 to 100:0)

1 a R^1 = Me, **b** R^1 = Ts; **5 a** R^2 = H,**b** R^2 = CN, **c** R^2 = *t*-Bu;
6 a R^3 = Me, R^4 = H, R^5 = Et; **b** R^3 = *i*-Bu, R^4 = H, R^5 = Me; **c** $R^3 + R^4 = (CH_2)_3$, R^5 = Me

Compound	R^1	R^2	R^3	R^4	R^5	Yield, %	*dr**
7a	Me	H	Me	H	Et	80	53:47
7b	Me	H	*i*-Bu	H	Me	75	70:30
7c	Me	CN	Me	H	Et	76	50:50
7d	Me	CN	*i*-Bu	H	Me	78	63:37
7e	Ts	*t*-Bu	*i*-Bu	H	Me	88	60:40
7f	Ts	H	$(CH_2)_3$		Me	91	100:0
7g	Ts	*t*-Bu	$(CH_2)_3$		Me	98	100:0

* Diastereomeric ratios were determined by ^{1}H NMR spectroscopy after chromatography on silica gel.

Compound **7g** crystallizes in the chiral triclinic space group *P*1 and the chromogenic butadiene chromophore adopts a coplanar *E*,*E*-configuration of the auxochrome–chromophore–antiauxochrome moiety. Furthermore, the aryl rings are arranged in an orthogonal orientation with respect to the chromophore plane and indicate an intramolecular π-stacking stabilizing the chromophore planarization. A closer inspection of the characteristic bond lengths of the push–pull chromophore system gives an insight in the bonding nature of the electronic ground state [57]. Most indicative for this class of chromophores is their tendency to bond length equilibration [58] causing an extended equidistribution of π-electron density by resonance [59]. In comparison to unsubstituted butadiene [60] where the double bonds possess bond lengths of 1.337 Å and the single bond of this simple conjugated diene displays a length of 1.476 Å, the formal double bonds C(21)–C(22) and C(23)–C(24) of structure **7h** are elongated to 1.353 and 1.396 Å, whereas the formal single bonds C(22)–C(23) and C(24)–C(25) are shortened to 1.415 und 1.432 Å, respectively. Thereby, a bond length alternation [61] of 0.05 Å can be determined, which lies significantly lower than for regular polyenes (0.11 Å), approaching the cyanine limit of 0.0 Å for an ideal merocyanine. In agreement with the theory the merocyanines **4** and **7a**–**g** are obviously very close to the ideal merocyanine in the electronic ground state.

Computations on the level of the semiempirical PM3 theory implementing the solvation energy model SM5.4/P [62] were performed for the diastereomers *E*,*E*-**7a** and *E*,*Z*-**7a** (for the computations only the methyl esters were considered) in order to understand which diastereomer is the energetically most stable and whether the observed product ratio is based upon a thermodynamically or kinetically controlled reaction (Fig. 2). Based upon the mechanistic rationale that intermediate ynylidene

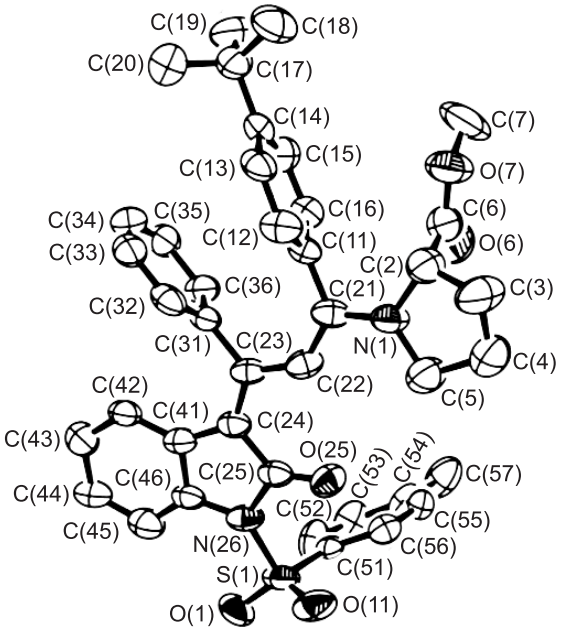


Fig. 1. Crystal structure of compound **7g**. Thermal ellipsoids are shown at the 50% probability level (hydrogen atoms are omitted)

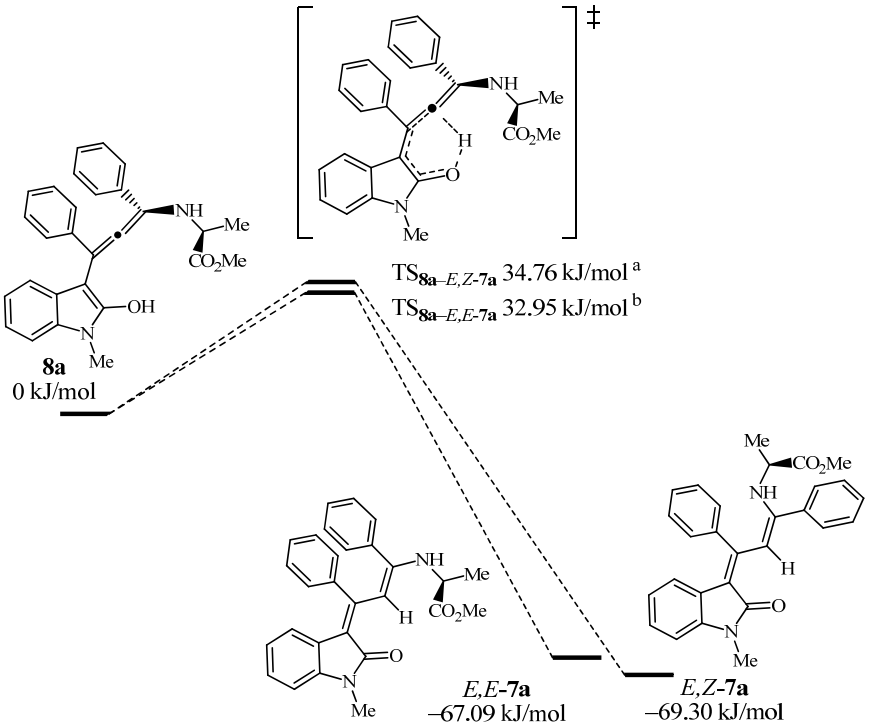


Fig. 2. Computed reaction profile for the final 1,5-H-shift of the elusive allenol intermediate **8a** to form the diastereomers *E*,*E*-**7a** and *E*,*Z*-**7a** (the methyl esters have been computed for simplicity). Imaginary frequencies for the respective transition states: [a] i1639 cm^{-1}; [b] i1549 cm^{-1}

Table 1

Selected absorption and emission data of the 3-amino acid ester-substituted prop-2-enylidene indolones 7a–g

Compound	Absorption, $\lambda_{max,abs}$, nm (ε, $l \cdot mol^{-1} \cdot cm^{-1}$)*	Absorption, $\lambda_{max,abs}$, nm (film)**	Emission, $\lambda_{max,em}$, nm (film)**	Stokes shift, $\Delta\tilde{\upsilon}$, cm^{-1}*** (film)
7a	442 (34900)	449	596	5500
7b	443 (35400)	445	595	5600
7c	433 (32400)	445	580	5200
7d	434 (32800)	447	579	5100
7e	446 (38500)	486 sh, 467	631	4800
7f	479 (43900), 465 sh (39500)	490, 465 sh	631	4600
7g	482 (40100), 466 sh (37600)	491 sh, 462	627	4600

* Recorded in CH_2Cl_2.
** Prepared by dropcasting.
*** $\Delta\tilde{\upsilon} = \lambda_{max,abs}^{-1} - \lambda_{max,em}^{-1}$.

indolones form upon the domino insertion-coupling sequence, which indeed can be isolated [53], the stepwise Michael addition of the L-amino acid ester should give an elusive allenol intermediate **8a**. A final, irreversible pericyclic 1,5-H-shift obviously furnishes, with the enol–ketone tautomerism as a thermodynamic driving force, the title compounds **7a**, which are 67.09 (*E*,*E*-**7a**) and 69.30 kJ/mol (*E*,*Z*-**7a**) lower in energy than the allenol precursor **8a**. According to the PM3 calculations the isomer *E*,*Z*-**7a** is by 2.21 kJ/mol slightly more stable than the isomer *E*,*E*-**7a**. By this computed energy difference the equilibrium distribution can be calculated to be 68:32 in favor of isomer *E*,*Z*-**7a**. The transition states $TS_{\mathbf{8a}\text{–}E,E\text{-}\mathbf{7a}}$ and $TS_{\mathbf{8a}\text{–}E,Z\text{-}\mathbf{7a}}$ were unambiguously verified by the appearance of single imaginary vibration frequencies for the 1,5-H-shift. The calculated transition state energy difference $\Delta\Delta G^{\ddagger}(TS_{\mathbf{8a}\text{–}E,E\text{-}\mathbf{7a}} - TS_{\mathbf{8a}\text{–}E,Z\text{-}\mathbf{7a}})$ is 1.81 kJ/mol, however, the energy of the transition state producing the less stable isomer *E*,*E*-**7a** is slightly lower, indicating that this process is very likely to be kinetically controlled. From the transition states energy difference the product ratio can be calculated to 65:35 in favor of isomer *E*,*E*-**7a**. Based upon the results obtained from the crystal structure of compound **7g**, which clearly supports the *E*,*E*-configuration, the diastereomeric ratios for the compounds **7a**–**e** can be accounted for by a kinetically controlled product formation.

All 3-amino acid ester-substituted prop-2-enylidene indolones **7a**–**g** are obtained as orange-red solids with strong broad absorption bands at 433–482 nm and molar extinction coefficients 32400–43900 $l \cdot mol^{-1} \cdot cm^{-1}$ in dichloromethane solutions. For dropcasted films, broad absorption bands are found at 445–491 nm (Table 1). As a consequence of their electronic absorption spectra the title compounds qualify as push–pull chromophores or merocyanines [63, 64], where the electronic fine tuning of the position of the absorption bands is predominantly influenced by indolone *N*-substituent and by the terminal amino acid moiety. As already found for the structurally related indolone merocyanines **4** the pyrrolidinyl moiety of the L-proline ester causes the most pronounced red shift in combination with the strongly electron withdrawing tosyl substituent on the indolone (Table 1, compounds **7f**,**g**). In the comparable series of the merocyanines **7a**–**d**, the effect of

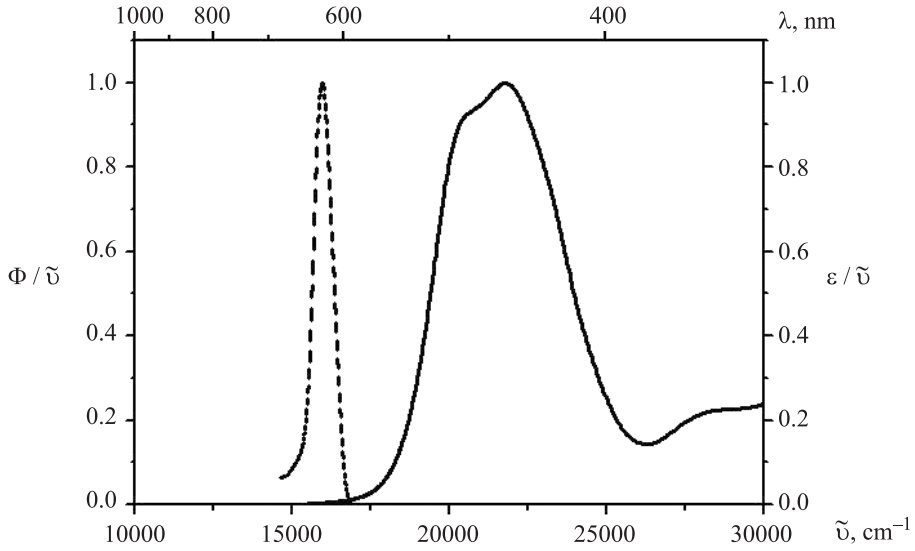


Fig. 3. Absorption (solid line) and emission (dashed line) spectrum of the dropcasted film of compound **7g** (recorded at room temperature, normalized spectra, $\lambda_{max,exc}$ = 490 nm)

the remote aryl substituent R^2 stemming from the alkyne coupling partner is fairly low indicating a dominance of nonconjugative interactions of the aryl substituent with the chromogenic push–pull system. The same is found for the absorption in film reproducing the solution data in a comparable range. However, for the *N*-tosyl-substituted indolone chromophores the bathochromic shift from solution to film is quite substantial, indicating a dominance of *J*-type aggregation (Table 1, compounds **7e**–**g**).

And as reported before, also the 3-amino acid-substituted prop-2-enylidene indolones **7a**–**g** are completely nonemissive in solution, yet, they display intense orange to red luminescence in the amorphous state (film) with sharp emission bands in a range from 579 to 631 nm (Fig. 3). The energy differences between longest wavelength absorption maxima and emission maxima are quite pronounced and the Stokes shifts range between 4600 and 5600 cm^{-1}. The redshifted absorption bands clearly indicate a *J*-aggregation [65] of the chromophores. Therefore, the observed sharp emission bands with narrow halfwidth bands is induced by *J*-aggregation [66, 67], which can be additionally rationalized by a splitting according to Davydov's exciton model [68].

In conclusion, we have expanded the consecutive three-component insertion–coupling–addition sequence giving 3-L-amino acid ester-substituted prop-2-enylidene indolones in good to excellent yields. While the primary amino acid esters, L-alanine ethylester and L-isoleucine methylester, lead to the formation of inseparable mixtures of the *E*,*E*- and *E*,*Z*-diastereomers as a consequence of the terminal chromogenic intramolecular 1,5-H-shift as supported by PM3 computations, the L-proline methylester furnishes selectively and exclusively the *E*,*E*-isomer. All representatives of these novel bioorganic push–pull chromophores display profound fluorescence in dropcasted films with large Stokes shifts, yet, they are completely nonemissive in solution. Further studies employing this diversity oriented synthetic methodology to oligopeptides as substrates, the aggregation of the resulting chromophores and their photophysical behavior are currently underway.

EXPERIMENTAL

IR spectra were recorded on Bruker Vector 22 FT-IR spectrometer in KBr discs. UV/vis spectra were recorded on Hewlett Packard HP8452 A Diode Array spectrophotometer in CH_2Cl_2 solution. Fluorescence spectra were recorded on Perkin-Elmer LS-55 spectrometer. ^{1}H NMR spectra were recorded on Bruker DRX-500 spectrometer (500 MHz), ^{13}C NMR spectra – on Bruker DRX-300 (75 MHz, compounds **7a**–**d**) and Bruker AC-300 (75 MHz, compounds **7e**–**g**) spectrometers. Solvent used for all NMR spectra – $CDCl_3$, internal standard – TMS. The assignments of quaternary carbon atoms, CH, CH_2 and CH_3 groups have been made by using 135-DEPT spectra. Mass spectra were recorded on Jeol JMS-700 (ionization method MALDI, compounds **7a**,**f**) and Finnigan TSQ 700 (ionization method EI, 70 eV, compounds **7b**–**e**,**g**) spectrometers. Elemental analyses were carried out in the microanalytical laboratories of the Institute of Pharmacy, Heinrich-Heine-Universität Düsseldorf. Melting points were determined on Büchi Melting Point B-540 apparatus and are uncorrected. Optical rotations of the compounds **7a**–**g** were measured with a Polarimeter 341 Perkin-Elmer (wavelength λ 589 nm) in CH_2Cl_2 solution. Column chromatography performed using silica gel 60 mesh 230–400 (Macherey-Nagel, Düren). TLC analysis performed using silica gel plates (60 F254 Merck, Darmstadt), eluent hexane–EtOAc, 4:1. All reactions involving palladium-copper catalysis were performed in degassed oxygen-free solvents under a nitrogen atmosphere using Schlenk and syringe techniques. $PdCl_2(PPh_3)_2$, CuI, and the L-amino acid esters **6a**–**c** were purchased from Acros and Aldrich (reagent grade) and used without further purification. Diisopropylethylamine was dried and distilled according to standard procedures [69]. Detailed preparative procedures including full analytics and ^{1}H, ^{13}C and 135-DEPT NMR spectra of the *ortho*-iodophenylanilides **1a**,**b** have been previously reported [52].

For the measurements of the optical properties, compounds **7a**–**g** were dissolved in CH_2Cl_2 for the preparation of films on glass by slow evaporation. For the UV/Vis measurements a thin film was dropcasted onto one side of the inner surface of a common glass cuvette. For the fluorescence measurements a thin film was dropcasted onto an object slide. The slide was placed into the cavity in a perpendicular orientation and with an 45° angle with respect to the optical pathway of a fluorescence spectrometer. The excitation wavelength was chosen in accordance to the longest absorption wavelength maximum as determined from the film UV/Vis spectra.

The consecutive three-component synthesis of 3-amino acid ester-substituted prop-2-enylidene indolones 7a–g (General Method). In a flame-dried and argon-flushed Schlenk tube iodophenylanilide **1a**,**b** (1.00 mmol), alkyne **5a**–**c** (1.10 mmol), and dry degassed THF (5 ml) were placed (for experimental details see Table 2). After the addition of $PdCl_2(PPh_3)_2$ (35 mg, 0.05 mmol), and CuI (10 mg, 0.05 mmol), diisopropylethylamine (1.7 ml, 10 mmol) was added to the reaction mixture, and the reaction mixture was stirred at room temperature for 16 h. Then, the amino acid ester hydrochloride **6a**–**c** (2.00 mmol), diisopropylethylamine (1.7 ml), and EtOH (2 ml) were added. Then, the sealed reaction vessel was placed in a thermostated oil bath at 80 °C and stirred for 48 h. After cooling to room temperature the solvents were removed *in vacuo* and the residue was chromatographed on silica gel (hexane–EtOAc) to give the 3-amino acid ester-substituted prop-2-enylidene indolones **7a**–**g** as orange solids.

(*S*)-Ethyl-2-{[3-(1-methyl-2-oxoindolin-3-ylidene)-1,3-diphenylprop-1-en-1-yl]-amino}propanoate (7a). The product was purified by column chromatography using hexane–EtOAc (4:1) as eluent. Orange solid, mp 117–119°C. $[\alpha]_D^{20}$ 13° (*c* 0.5 mg/ml). IR spectrum, ν, cm^{-1}: 609, 646, 665, 694, 713, 731, 744, 765, 815, 916, 947, 970, 1001, 1016, 1049, 1082, 1111, 1122, 1151, 1178, 1211, 1249, 1278, 1294, 1332, 1373, 1421, 1442, 1471, 1487, 1504, 1543, 1604, 1666, 1726, 2889, 2978, 3051. UV/Vis spectrum, λ_{max}, nm (ε): 442 (34900). ^{1}H NMR spectrum, δ, ppm (*J*, Hz) (diastereomer ratio 53:47): (*E*,*E*)-isomer: 0.78 (1.59H, d, *J* = 7.0, NHCHC$\underline{H}_3$); 1.13 (1.59H, t, *J* = 7.1, OCH$_2$C$\underline{H}_3$); 3.24 (1.59H, s, 1-CH$_3$); 3.64–3.75 (0.53H, m, NHC$\underline{H}$Me); 3.93–4.02 (1.06H, m, OC$\underline{H}_2$CH$_3$); 5.60 (0.53H, d, *J* = 7.4, NH); 6.52 (0.53H, dt, *J* = 7.7, *J* = 1.1, H Ind); 6.71 (1.06H, d, *J* = 7.7, H Ph);

Table 2

Experimental details of the three-component synthesis of 3-L-amino acid ester-substituted prop-2-enylidene indolones 7a–g

ortho-Iodo-alkynylanilide	Alkyne	Amino acid ester hydrochloride	Amino acid ester-substituted prop-2-enylidene indolone (isolated yield)
1a (361 mg, 1.00 mmol)	**5a** (112 mg, 1.10 mmol)	**6a** (307 mg, 2.00 mmol)	**7a** (362 mg, 80%)
1a (361 mg, 1.00 mmol)	**5a** (112 mg, 1.10 mmol)	**6b** (363 mg, 2.00 mmol)	**7b** (360 mg, 75%)
1a (361 mg, 1.00 mmol)	**5b** (140 mg, 1.10 mmol)	**6a** (307 mg, 2.00 mmol)	**7c** (363 mg, 76%)
1a (361 mg, 1.00 mmol)	**5b** (140 mg, 1.10 mmol)	**6b** (363 mg, 2.00 mmol)	**7d** (394 mg, 78%)
1b (501 mg, 1.00 mmol)	**5c** (174 mg, 1.10 mmol)	**6b** (363 mg, 2.00 mmol)	**7e** (595 mg, 88%)
1b (501 mg, 1.00 mmol)	**5a** (112 mg, 1.10 mmol)	**6c** (331 mg, 2.00 mmol)	**7f** (550 mg, 91%)
1b (501 mg, 1.00 mmol)	**5c** (174 mg, 1.10 mmol)	**6c** (331 mg, 2.00 mmol)	**7g** (648 mg, 98%)

6.88–7.01 (6H, m, H Ph, C<u>H</u>=C(Ph)NH)*; 7.31–7.35 (2H, m, H Ph, C<u>H</u>=C(Ph)NH)*; 7.37–7.49 (4H, m, H Ind, H Ph)*; 7.55–7.59 (1H, m, H Ph)*; additional signals for the (*E*,*Z*)-isomer: 1.30 (1.41H, t, *J* = 7.1, NHCHC<u>H</u>$_3$); 1.65 (1.41H, d, *J* = 6.9, OCH$_2$C<u>H</u>$_3$); 3.18–3.24 (0.47H, m, NHC<u>H</u>Me); 3.32 (1.41H, s, 1-CH$_3$); 4.21–4.20 (0.94H, m, OC<u>H</u>$_2$CH$_3$); 5.48 (0.47H, d, *J* = 7.4, NH); 6.44 (0.47H, dt, *J* = 7.7, *J* = 1.1, H Ind). ^{13}C NMR spectrum, δ, ppm: (*E*,*E*)-isomer: 14.3 (CH$_3$); 18.5 (CH$_3$); 25.8 (CH); 51.9 (CH$_3$); 61.1 (CH$_2$); 101.1 (CH); 107.0 (CH); 114.7 (C); 120.7 (CH); 121.7 (CH); 124.6 (C); 125.2 (CH); 127.3 (CH); 127.7 (CH); 128.1 (CH); 128.4 (CH); 128.6 (CH); 128.7 (CH); 129.1 (CH); 129.2 (CH); 129.6 (CH); 129.9 (CH); 137.9 (C); 140.5 (C); 149.6 (C); 155.7 (C); 156.7 (C); 168.2 (C); 172.7 (C); signals for the (*E*,*Z*)-isomer: 14.4 (CH$_3$); 19.1 (CH$_3$); 25.9 (CH); 53.2 (CH$_3$); 61.9 (CH$_2$); 103.9 (CH); 107.2 (CH); 116.1 (C); 120.9 (CH); 121.7 (CH); 124.9 (C); 126.1 (CH); 127.6 (CH); 128.0 (CH); 128.4 (CH); 128.6 (CH); 128.8 (CH); 129.3 (CH); 129.7 (CH); 130.4 (CH); 130.5 (CH); 133.3 (CH); 138.5 (C); 139.6 (C); 141.2 (C); 151.9 (C); 156.9 (C); 167.6 (C); 173.5 (C). Mass spectrum, *m*/*z*: 452 [M]$^+$. Found: C 75.70; H 6.26; N 5.85. $C_{29}H_{28}N_2O_3 \cdot 0.33H_2O$. Calculated, %: C 75.96; H 6.30; N 6.11.

(*S*)-Methyl-4-methyl-2-{[3-(1-methyl-2-oxoindolin-3-ylidene)-1,3-diphenylprop-1-en-1-yl]amino}pentanoate (7b). The product was purified by column chromatography using hexane–EtOAc (4:1) as eluent. Orange solid, mp 132–135°C. $[\alpha]_D^{20}$ 7° (*c* 0.5 mg/ml). IR spectrum, ν, cm^{-1}: 615, 655, 698, 719, 732,746, 773, 833, 846, 894, 918, 975, 1001, 1026, 1049, 1083, 1126, 1155, 1166, 1188, 1209, 1224, 1247, 1286, 1296, 1319, 1334, 1381, 1417, 1440, 1460, 1469, 1485, 1512, 1556, 1581, 1606, 1662, 1730, 2953, 3020, 3051. UV/Vis spectrum, λ_{max}, nm (ε): 443 (35400). ^{1}H NMR spectrum, δ, ppm (*J*, Hz) (diastereomer ratio 70:30): (*E*,*E*)-isomer: 0.61 (2.1H, d, *J* = 6.5) and 0.68 (2.1H, d, *J* = 6.6, CH$_2$CH(C<u>H</u>$_3$)$_2$); 0.98 (2.1H, m, C<u>H</u>$_2$C<u>H</u>Me$_2$); 3.24 (2.1H, s, 1-CH$_3$); 3.52 (2.1H, s, COOCH$_3$); 5.59 (0.7H, td, *J* = 7.7, *J* = 1.0, NHC<u>H</u>COOMe); 6.52 (0.7H, d, *J* = 7.5, NH); 6.70 (1H, dd, *J* = 7.8, *J* = 3.9, H Ind)*; 6.89–7.02 (3.5H, m, H Ind, H Ph, C<u>H</u>=C(Ph)NH)*; 7.31–7.37 (3.5H, m, H Ind, H Ph)*; 7.42–7.51 (2.5H, m, H Ind, H Ph)*; 7.57–7.64 (4.5H, m, H Ind, H Ph)*; additional signals for the (*E*,*Z*)-isomer: 0.71–0.79 (0.9H, m) and 1.07 (0.9H, ddd, *J* = 13.7, *J* = 8.8, *J* = 4.9, CH$_2$CH(C<u>H</u>$_3$)$_2$); 1.29–1.39 (0.9H, m, C<u>H</u>$_2$C<u>H</u>Me$_2$); 3.30 (0.9H, s, 1-CH$_3$); 3.64 (0.9H, s, COOCH$_3$); 5.47 (0.3H, d, *J* = 7.6, NH); 6.43 (0.3H, d, *J* = 7.7, NH). ^{13}C NMR spectrum, δ, ppm: (*E*,*E*)-isomer: 21.6 (CH$_3$); 22.9 (CH$_3$); 24.5 (CH);

* Overlapping signals of both isomers (here and below).

25.7 (CH_3); 41.5 (CH_2); 52.1 (CH); 55.3 (CH_3); 102.7 (CH); 107.0 (CH); 115.6 (C); 120.6 (CH); 121.6 (CH); 124.6 (C); 126.0 (CH); 127.8 (CH); 128.1 (CH); 128.4 (CH); 128.6 (CH); 129.2 (CH); 130.3 (CH); 138.4 (C); 139.7 (C); 140.9 (C); 152.0 (C); 157.1 (C); 168.2 (C); 173.2 (C); additional signals for the (*E*,*Z*)-isomer: 22.7 (CH_3); 23.0 (CH_3); 25.2 (CH); 25.9 (CH_3); 42.9 (CH_2); 52.6 (CH); 56.1 (CH_3); 107.2 (CH); 120.9 (CH); 121.7 (CH); 127.5 (CH); 128.0 (CH); 128.3 (CH); 128.5 (CH); 129.0 (CH); 129.6 (CH); 130.6 (CH); 140.6 (C); 141.1 (C); 174.0 (C). Mass spectrum, *m*/*z* (I_{rel}, %): 480 $[M]^+$ (9), 435 $[M–CH_3–CH_2O]^+$ (9), 351 $[M–C_5H_{10}CO_2Me]^+$ (17), 336 $[M–NHC_5H_{10}CO_2Me]^+$ (22), 286 $[C_{19}H_{12}NO_2]^+$ (30), 262 $[C_{18}H_{16}NO]^+$ (26), 234 $[M–NHC_5H_{10}CO_2Me–PhCCH]^+$ (26), 190 $[C_{11}H_{12}NO_2]^+$ (14), 120 $[C_8H_{10}N]^+$ (13), 105 $[C_7H_7N]^+$ (100). Found, %: C 76.01; H 6.39; N 5.57. $C_{31}H_{32}N_2O_3·0.5H_2O$. Calculated, %: C 76.05; H 6.79; N 5.72.

(*S*)-Ethyl-2-{[1-(4-cyanophenyl)-3-(1-methyl-2-oxoindolin-3-ylidene)-3-phenylprop-1-en-1-yl]amino}propanoate (7c). The product was purified by column chromatography using hexane–EtOAc (7:3) as eluent. Orange solid, mp 166–169°C. $[\alpha]_D^{20}$ 11° (*c* 0.5 mg/ml). IR spectrum, ν, cm^{-1}: 626, 648, 657, 696, 711, 732, 750, 781, 833, 844, 989, 1014, 1051, 1083, 1107, 1126, 1155, 1172, 1211, 1253, 1273, 1286, 1311, 1334, 1379, 1415, 1448, 1467, 1500, 1516, 1535, 1573, 1600, 1670, 1720, 2223, 2802, 2875, 2931, 2978, 3026. UV/Vis spectrum, λ_{max}, nm (ε): 433 (32400). ^{1}H NMR spectrum, δ, ppm (*J*, Hz) (diastereomer ratio 50:50): (*E*,*E*)-isomer: 0.79 (1.5H, d, *J* = 7.0, NHCHC<u>H</u>$_3$); 1.13 (1.5H, t, *J* = 7.1, $OCH_2C\underline{H}_3$); 3.24 (1.5H, s, 1-CH_3); 3.99 (0.5H, td, *J* = 7.2, *J* = 3.7, NHC<u>H</u>Me); 4.53 (1H, dq, *J* = 6.9, *J* = 3.5, O<u>C</u>$\underline{H}_2CH_3$); 5.51 (0.5H, d, *J* = 7.5, NH); 6.50 (1H, m, H Ind)*; 6.71 (1H, d, *J* = 7.8, C<u>H</u>=C(Ar)NH)*; 6.83–6.87 (1H, m, H Ind)*; 6.94–7.01 (2H, m, H Ph)*; 7.03–7.07 (2H, m, H Ar)*; 7.17–7.22 (1H, m, H Ind)*; 7.48–7.69 (6H, m, H Ph, H Ar, H Ind)*; additional signals for the (*E*,*Z*)-isomer: 1.31 (1.5H, d, *J* = 7.1, NHCHC<u>H</u>$_3$); 1.64 (1.5H, t, *J* = 6.9, $OCH_2C\underline{H}_3$); 3.30 (1.5H, s, 1-CH_3); 3.48–3.56 (0.5H, m, NHC<u>H</u>Me); 4.26 (1H, dq, *J* = 7.2, *J* = 3.6, O<u>C</u>$\underline{H}_2CH_3$); 5.64 (0.5H, d, *J* = 7.7, NH). ^{13}C NMR spectrum, δ, ppm: (*E*,*E*)-isomer: 14.3 (CH_3); 18.4 (CH_3); 25.8 (CH_3); 52.0 (CH); 61.3 (CH_2); 102.2 (CH); 107.2 (CH); 111.9 (C); 116.2 (C); 118.4 (C); 120.9 (CH); 122.0 (CH); 124.1 (C); 126.0 (CH); 128.0 (CH); 128.3 (CH); 128.5 (CH); 129.3 (CH); 130.0 (CH); 130.5 (CH); 131.4 (CH); 139.4 (C); 141.1 (C); 142.6 (C); 150.5 (C); 153.4 (C); 168.2 (C); 172.3 (C); signals for the (*E*,*Z*)-isomer: 14.4 (CH_3); 18.9 (CH_3); 25.9 (CH_3); 53.2 (CH); 62.0 (CH_2); 105.8 (CH); 107.5 (CH); 112.7 (C); 116.2 (C); 118.7 (C); 121.2 (CH); 122.2 (CH); 124.4 (C); 127.0 (CH); 128.1 (CH); 128.4 (CH); 129.2 (CH); 129.8 (CH); 130.4 (CH); 130.6 (CH); 132.5 (CH); 139.9 (C); 141.7 (C); 143.4 (C); 153.4 (C); 153.5 (C); 168.5 (C); 172.4 (C). Mass spectrum, *m*/*z* (I_{rel}, %): 477 $[M]^+$ (45), 404 $[M–CO_2C_2H_5]^+$ (13), 376 $[M–CH_3CHCO_2C_2H_5]^+$ (81), 361 $[M–NHCH_3CHCO_2C_2H_5]^+$ (100), 331 $[C_{21}H_{19}N_2O_2]^+$ (14), 316 $[C_{20}H_{16}N_2O_2]^+$ (10), 285 $[C_{19}H_{13}N_2O]^+$ (19), 261 $[C_{17}H_{13}N_2O]^+$ (38), 245 $[C_{17}H_{11}NO]^+$ (15), 234 $[C_{16}H_{12}NO]^+$ (47), 201 $[C_{16}H_9]^+$ (35), 180 $[C_{12}H_8N_2]^+$ (21), 173 $[C_{11}H_{11}NO]^+$ (18), 165 $[C_{11}H_5N_2]^+$ (13), 158 $[C_{10}H_8NO]^+$ (13), 146 $[C_9H_8NO]^+$ (32), 130 $[C_9H_6O]^+$ (32), 105 $[C_7H_7N]^+$ (18). Found, %: C 74.66; H 5.56; N 8.73. $C_{30}H_{27}N_3O_3·0.33H_2O$. Calculated, %: C 74.52; H 5.77; N 8.69.

(*S*)-Methyl-2-{[(1-(4-cyanophenyl)-3-(1-methyl-2-oxoindolin-3-ylidene)-3-phenylprop-1-en-1-yl]amino}-4-methylpentanoate (7d). The product was purified by column chromatography using hexane–EtOAc (7:3) as eluent. Orange solid, mp 138–142°C. $[\alpha]_D^{20}$ 8° (*c* 0.5 mg/ml). IR spectrum, ν, cm^{-1}: 623, 646, 673, 698, 731, 746, 785, 815, 844, 867, 916, 937, 964, 997, 1016, 1053, 1087, 1109, 1128, 1155, 1188, 1199, 1242, 1255, 1273, 1294, 1334, 1379, 1400, 1417, 1435, 1469, 1490, 1519, 1573, 1606, 1662, 1699, 1734, 2225, 2872, 2929, 2956, 3049. UV/Vis spectrum, λ_{max}, nm (ε): 434 (32800). ^{1}H NMR spectrum, δ, ppm (*J*, Hz) (diastereomer ratio 63:37): (*E*,*E*)-isomer: 0.63 (1.89H, d, *J* = 6.5) and 0.68 (1.89H, d, *J* = 6.6, $CH_2CH(C\underline{H}_3)_2$); 0.94–1.00 (1.89H, m, $C\underline{H}_2C\underline{H}Me_2$); 3.23 (1.89H, s, 1-$CH_3$); 3.52 (1.89H, s, $COOCH_3$); 5.63 (0.63H, t, *J* = 7.7, $Me_2CHCH_2C\underline{H}NHCOOMe$); 6.53 (0.63H, d, *J* = 7.4, NH); 6.66–6.76 (2H, m, H Ind, C<u>H</u>=C(Ar)NH)*; 6.92–7.08 (4H, m, H Ind, H Ph)*; 7.47–7.66 (7H, m, H Ind, H Ph, H Ar)*; 7.89 (0.63H, d, *J* = 8.6, H Ind); additional signals for the (*E*,*Z*)-isomer: 0.69–0.79 (1.11H, m) and 1.08 (1.11H, m, $CH_2CH(C\underline{H}_3)_2$); 1.21–1.36 (1.11H, m, $C\underline{H}_2C\underline{H}Me_2$); 3.29 (1.11H, s, 1-$CH_3$); 3.84 (1.11H, s,

$COOCH_3$); 5.51 (0.37H, t, J = 7.7, $Me_2CHCH_2C\underline{H}NHCOOMe$); 6.45 (0.37H, d, J = 7.4, NH); 7.69–7.74 (0.37H, m, H Ind). ^{13}C NMR spectrum, δ, ppm: (*E*,*E*)-isomer: 21.7 (CH_3); 23.0 (CH_3); 25.2 (CH); 25.8 (CH_3); 41.4 (CH_2); 52.2 (CH); 55.3 (CH_3); 102.9 (CH); 107.2 (CH); 111.9 (C); 116.7 (C); 118.6 (C); 120.9 (CH); 122.0 (CH); 124.1 (C); 126.1 (CH); 127.9 (CH); 128.3 (CH); 128.8 (CH); 129.2 (CH); 129.5 (CH); 130.1 (CH); 130.4 (CH); 131.5 (CH); 132.7 (CH); 139.5 (C); 141.3 (C); 142.7 (C); 150.6 (C); 153.8 (C); 168.2 (C); 173.6 (C); additional signals for the (*E*,*Z*)-isomer: 22.8 (CH_3); 24.5 (CH_3); 25.3 (CH); 25.9 (CH_3); 42.7 (CH_2); 52.7 (CH); 56.1 (CH_3); 104.6 (CH); 107.5 (CH); 112.7 (C); 118.7 (C); 121.2 (CH); 122.1 (CH); 124.3 (C); 126.9 (CH); 128.0 (CH); 128.6 (CH); 129.2 (CH); 129.4 (CH); 129.8 (CH); 130.3 (CH); 130.7 (CH); 132.5 (CH); 132.7 (CH); 140.0 (C); 141.6 (C); 143.3 (C); 153.2 (C); 154.1 (C); 168.4 (C); 173.9 (C). Mass spectrum, *m*/*z* (I_{rel}, %): 505 $[M]^+$ (1), 376 $[M–C_5H_{10}CO_2Me]^+$ (3), 361 $[M–NHC_5H_{10}CO_2Me]^+$ (6), 215 $[C_{12}H_{11}N_2O_2]^+$ (21), 173 $[C_{10}H_7NO_2]^+$ (18), 147 $[C_9H_9NO]^+$ (10), 130 $[C_5H_{11}CO_2Me]^+$ (100), 105 $[C_7H_7N]^+$ (22). Found, %: C 75.53; H 6.00; N 8.14. $C_{32}H_{31}N_3O_3$. Calculated, %: C 76.02; H 6.18; N 8.31.

(*S*)-Methyl-2-{[1-(4-(*tert*-butyl)phenyl)-3-(2-oxo-1-tosylindolin-3-ylidene)-3-phenylprop-1-en-1-yl]amino}-4-methylpentanoate (7e). The product was purified by column chromatography using hexane–EtOAc (4:1) as eluent. Orange solid, mp 168–173°C. $[\alpha]_D^{20}$ 13° (*c* 0.5 mg/ml). IR spectrum, ν, cm^{-1}: 644, 661, 680, 690, 702, 717, 740, 777, 812, 833, 850, 902, 931, 962, 981, 1002, 1045, 1076, 1132, 1157, 1168, 1205, 1244, 1274, 1292, 1315, 1357, 1404, 1433, 1452, 1465, 1487, 1500, 1550, 1570, 1595, 1691, 1732, 2872, 2933, 2954, 2962. UV/Vis spectrum, λ_{max}, nm (ε): 446 (38500). ^{1}H NMR spectrum, δ, ppm (*J*, Hz) (diastereomer ratio 60:40): (*E*,*E*)-isomer: 0.66 (3.6H, m, $CH_2CH(C\underline{H}_3)_2$); 0.94–1.01 (3H, m, $C\underline{H}_2C\underline{H}Me_2$)*; 1.31 (5.4H, s, $C(CH_3)_3$); 2.36 (1.8H, s, $ArCH_3$); 3.52 (1.8H, s, $COOCH_3$); 3.68–3.73 (0.6H, m, $NHC\underline{H}COOMe$); 5.53 (0.6H, d, J = 8.0, NH); 6.60 (0.6H, t, J = 7.7, H Ind); 6.77 (0.6H, d, J = 7.2, H Ind); 6.83–6.95 (5H, m, H Ind, H Ar, $C\underline{H}$=C(Ar)NH, H Ts)*; 7.00 (0.6H, t, J = 7.8, H Ph); 7.10 (0.6H, s, $C\underline{H}$=C(Ar)NH); 7.29 (1.2H, d, J = 8.0, H Ph); 7.29–7.39 (1.8H, m, H Ph)*; 7.51 (0.6H, dd, J = 5.7, J = 3.3, H Ind); 7.58 (1.2H, d, J = 8.2, H Ts); 7.95 (1.2H, d, J = 8.2, H Ts); 8.03 (0.6H, d, J = 8.1, H Ind); additional signals for the (*E*,*Z*)-isomer: 0.56 (2.4H, m, $CH_2CH(C\underline{H}_3)_2$); 1.17 (3.6H, s, $C(CH_3)_3$); 2.41 (1.2H, s, $ArC\underline{H}_3$); 3.83 (1.2H, s, $COOCH_3$); 4.15–4.27 (0.4H, m, $NHC\underline{H}COOMe$); 5.42 (0.4H, d, J = 7.6, NH); 6.51 (0.4H, t, J = 7.6, H Ind); 7.20–7.25 (2.4H, m, H Ar, H Ts); 7.81–7.95 (1.2H, m, H Ar, H Ind). ^{13}C NMR spectrum, δ, ppm: (*E*,*E*)-isomer: 21.5 (CH_3); 21.9 (CH_3); 22.8 (CH_3); 22.7 (CH); 24.4 (CH_3); 31.2 (C); 42.9 (CH_2); 52.2 (CH); 55.3 (CH_3); 102.6 (CH); 111.3 (C); 112.8 (CH); 121.2 (CH); 123.3 (CH); 124.7 (CH); 125.3 (CH); 125.6 (CH); 126.1 (C); 127.9 (CH); 128.0 (C); 128.1 (CH); 129.3 (CH); 129.7 (CH); 131.1 (CH); 134.6 (C); 136.7 (C); 139.0 (C); 144.9 (C); 152.9 (C); 156.3 (C); 160.2 (C); 165.8 (C); 172.8 (C); additional signals for the (*E*,*Z*)-isomer: 21.9 (CH_3); 31.4 (C); 52.8 (CH); 125.9 (CH); 126.3 (C); 128.2 (CH); 129.3 (CH); 129.8 (CH); 135.8 (C); 136.8 (C); 140.2 (C); 154.6 (C); 156.4 (C). Mass spectrum, *m*/*z* (I_{rel}, %): 676 $[M]^+$ (8), 619 $[M–t\text{-}Bu]^+$ (39), 532 $[M–NHC_5H_{10}CO_2Me]^+$ (26), 521 $[M–SO_2C_6H_4CH_3]^+$ (37), 463 $[M–NSO_2C_6H_4CH_3–CH_3CH_2CH_3]^+$ (16), 422 $[M–C_6H_5–C_6H_4Bu\text{-}t–CH_3CH_2CH_3]^+$ (21), 405 $[C_{27}H_{19}NO_3]^+$ (39), 393 $[C_{27}H_{25}N_2O]^+$ (26), 377 $[M–NHC_5H_{10}CO_2Me–SO_2C_6H_4CH_3]^+$ (67), 362 $[C_{20}H_{14}N_2O_3S]^+$ (23), 349 $[C_{23}H_{27}NO_2]^+$ (16), 331 $[C_{24}H_{29}N]^+$ (26), 288 $[C_{18}H_{26}NO_2]^+$ (74), 167 $[C_{11}H_5NO]^+$ (28), 155 $[SO_2C_6H_4CH_3]^+$ (31), 132 $[C_8H_6NO]^+$ (37). Found, %: C 72.57; H 6.87; N 3.69. $C_{41}H_{44}N_2O_5S$. Calculated, %: C 72.75; H 6.55; N 4.14.

(*S*)-Methyl-1-[(1*E*,3*E*)-3-(2-oxo-1-tosylindolin-3-ylidene)-1,3-diphenylprop-1-en-1-yl]-pyrrolidine-2-carboxylate (7f). The product was purified by column chromatography using hexane–EtOAc (4:1) as eluent. Orange solid, mp 196–199°C. $[\alpha]_D^{20}$ 345° (*c* 0.25 mg/ml). IR spectrum, ν, cm^{-1}: 605, 634, 655, 688, 700, 738, 769, 813, 850, 894, 906, 933, 958, 972, 995, 1018, 1043, 1066, 1093, 1114, 1136, 1166, 1093, 1114, 1136, 1166, 1242, 1292, 1311, 1346, 1367, 1419, 1452, 1490, 1512, 1693, 1739, 2949, 3062. UV/Vis spectrum, λ_{max}, nm (ε): 479 (43900), 465 (39500, sh). ^{1}H NMR spectrum, δ, ppm (*J*, Hz) (diastereomer ratio 100:0): 1.52–2.26 (6H, m, $(CH_2)_3$); 2.39 (3H, s, $ArC\underline{H}_3$); 3.43 (3H, s, $COOCH_3$); 3.63–4.11 (1H, m, CHCOOMe); 5.14 (1H, s, $C\underline{H}$=CPhNH); 6.47 (2H, t, J = 7.6, H Ph); 6.65–6.99

(11H, m, H Ind, H Ph); 7.28 (2H, d, J = 8.2, H Ts); 7.85 (1H, d, J = 8.1, H Ind); 8.02 (2H, d, J = 8.2, H Ts). ^{13}C NMR spectrum, δ, ppm: 21.9 (CH_3); 23.7 (CH_2); 26.9 (CH_2); 30.6 (CH); 30.7 (CH_2); 52.3 (CH_3); 110.0 (C); 112.5 (CH); 121.1 (CH); 123.0 (CH); 124.8 (CH); 126.5 (C); 127.4 (CH); 127.6 (CH); 127.9 (CH); 128.0 (CH); 128.1 (CH); 128.3 (CH); 129.0 (CH); 129.1 (CH); 129.7 (CH); 135.2 (C); 137.0 (C); 139.5 (C); 144.7 (C); 153.1 (C); 154.8 (C); 158.8 (C); 165.9 (C); 173.0 (C). Mass spectrum, *m*/*z*: 604 $[M]^+$. Calculated, %: C 70.80; H 5.39; N 4.59. $C_{36}H_{32}N_2O_5S \cdot 0.33H_2O$. Found, %: C 71.02; H 5.60; N 4.50.

(S)-Methyl-1-[(1*E*,3*E*)-1-(4-(*tert*-butyl)phenyl)-3-(2-oxo-1-tosylindolin-3-ylidene)-3-phenylprop-1-en-1-yl]pyrrolidine-2-carboxylate (7g). The product was purified by column chromatography using hexane–EtOAc (4:1) as eluent. Orange solid, mp 184–186°C. $[\alpha]_D^{20}$ 379° (*c* 0.25 mg/ml). IR spectrum, ν, cm^{-1}: 655, 673, 688, 704, 725, 746, 777, 802, 817, 833, 856, 896, 910, 921, 960, 977, 1001, 1022, 1045, 1072, 1118, 1159, 1165, 1201, 1244, 1294, 1311, 1338, 1350, 1386, 1435, 1452, 1473, 1489, 1506, 1674, 1745, 2868, 2902, 2953. UV/Vis spectrum, λ_{max}, nm (ε): 482 nm (40100), 466 (37600, sh). ^{1}H NMR spectrum, δ, ppm (*J*, Hz) (diastereomer ratio 100:0): 1.18 (9H, s, $C(CH_3)_3$); 1.44–2.18 (6H, m, $(CH_2)_3$); 2.40 (3H, s, $ArC\underline{H}_3$); 3.39 (3H, s, $COOCH_3$); 3.74–3.90 (1H, m, C<u>H</u>COOMe); 5.11 (1H, m, C<u>H</u>=C(Ar)NH); 6.46 (2H, t, J = 7.7, H Ar); 6.56–6.96 (10H, m, H Ind, H Ar, H Ph); 7.28 (2H, d, J = 8.1, H Ts); 7.85 (1H, d, J = 8.2, H Ind); 8.01 (2H, d, J = 8.1, H Ts). ^{13}C NMR spectrum, δ, ppm: 21.9 (CH_3); 25.5 (CH_2); 27.1 (CH_2); 31.2 (CH_2); 31.3 (CH_3); 34.6 (C); 34.9 (CH); 52.1 (CH_3); 109.7 (C); 112.5 (CH); 121.1 (CH); 123.0 (CH); 124.4 (CH); 124.7 (CH); 124.8 (CH); 126.7 (CH); 127.3 (CH); 127.9 (CH); 128.2 (CH); 128.7 (C); 129.0 (CH); 129.7 (CH); 130.4 (C); 135.1 (C); 137.0 (C); 139.5 (C); 144.6 (C); 150.2 (C); 150.7 (C); 159.0 (C); 166.0 (C); 173.1 (C). Mass spectrum, *m*/*z* (I_{rel}, %): 660 $[M]^+$ (35), 532 $[M–NC_4H_7CO_2Me]^+$ (5), 505 $[M–TolSO_2]^+$ (28), 446 $[M–TolSO_2–CO_2Me]^+$ (17), 445 $[M–TolSO_2–HCO_2Me]^+$ (48), 389 $[M–TolSO_2–HCO_2Me–Me_2C{=}CH_2]^+$ (48), 374 $[M–NC_4H_7CO_2Me–t\text{-}BuC_6H_4CCH]^+$ (100), 362 $[M–TolSO_2–CH_3CHCO_2Me–Me_2C{=}CH_2]^+$ (21), 304 (11), 207 (10), 170 $[TolSO_2NH]^+$ (13), 128 $[NC_4H_7CO_2Me]^+$ (12). Found, %: C 72.91; H 6.52; N 3.94. $C_{40}H_{40}N_2O_5S$. Calculated, %: C 72.70; H 6.10; N 4.24.

X-Ray structural investigation of compound 7g (crystallosolvate with $CHCl_3$). Empirical formula: $C_{40}H_{40}N_2O_5S \cdot 0.5CHCl_3$; M 720.48 g/mol. Crystals – red plates; crystal size 0.38 × 0.16 × 0.08 mm^3; crystal system triclinic; space group *P*1 (chiral). Wavelength 0.71073 Å; at 200(2) K: *a* 11.1868(9), *b* 11.3135(9) *c* 15.2467(12) Å; α 84.531(2), β 77.392(2), γ 82.291(2)°; *V* 1861.7(3) $Å^3$; *Z* 2; d_{calc} 1.28 g/cm^3. Absorption coefficient 0.24 mm^{-1}; θ 2.1–23.3°; $-12 \le h \le 12$, $-12 \le k \le 12$, $-16 \le l \le 16$; 13300 reflections collected, independent reflections 10479 (R_{int} 0.0193), observed reflections 8387 ($I > 2\sigma(I)$). Absorption correction: semi-empirical from equivalents; max. and min. transmission: 0.98 and 0.91; refinement method: full-matrix least-squares on F^2; data / restraints / parameters: 10479 / 429 / 891; *GOOF* on F^2: 1.27; final *R* indices ($I > 2\sigma(I)$); R_1 0.076, wR_2 0.193; absolute structure parameter: –0.21(12); largest diff. peak and hole: 0.48 and –0.54 $eÅ^{-3}$. Crystallographic data has been deposited at the Cambridge Crystallographic Data Center (deposit CCDC 930694).

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