REACTIONS OF ETHYL (*Z*)-2-[2,2-BIS(ETHOXYCARBONYL)VINYL]-AMINO-3-DIMETHYLAMINOPROPENOATE WITH *C*-NUCLEOPHILES. SYNTHESIS OF SUBSTITUTED 3-AMINO-2*H*-PYRAN-2-ONES

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Dedicated to Professor Miha Tišler, University of Ljubljana, Ljubljana, Slovenia, on the occasion of his 70th birthday

Abstract - The reactions of ethyl (*Z*)-2-[2,2-bis(ethoxycarbonyl)vinyl]amino-3-dimethylaminopropenoate (**1**) with *C*-nucleophiles, such as β-keto esters (**2**, **4**, **6**), cyclic 1,3-diketones (**8a-e**), aromatic hydroxy compounds (**10**, **12**, **14**, **16** and **18**), and heterocyclic hydroxy compounds (**20**, **22**, **24**, **26** and **28**) gave 2*H*-pyran-2-ones (**3**, **5**, **7**), tetrahydrobenzopyranones (**9a-c**), benzopyranone (**11**), naphthopyranones (**13**, **15**, **17** and **19**), pyranopyranone (**21**), pyranobenzopyranone (**23**), pyranopyridinone (**25**), pyranoquinolinone (**27**), and pyranopyridazinone (**29**) derivatives.

Recently, synthesis of various derivatives of 2*H*-pyran-2-one and fused pyran-2-one has arisen an interest as nonpeptide HIV proteaze inhibitors. [1-9] There are many methods for the construction of these types of systems described in the literature. [10,11]

In connection with our studies of 2-acyl- (or 2-acylamino)-3-dimethylaminopropenoates as versatile reagents for the preparation of various heterocyclic systems [12-17] we prepared recently ethyl (*Z*)-2-[2,2-

bis(ethoxycarbonyl)vinyl]amino-3-dimethylaminopropenoate (**1**) as a reagent for the preparation of fused azolo-pyranones and pyranoazines. [14]

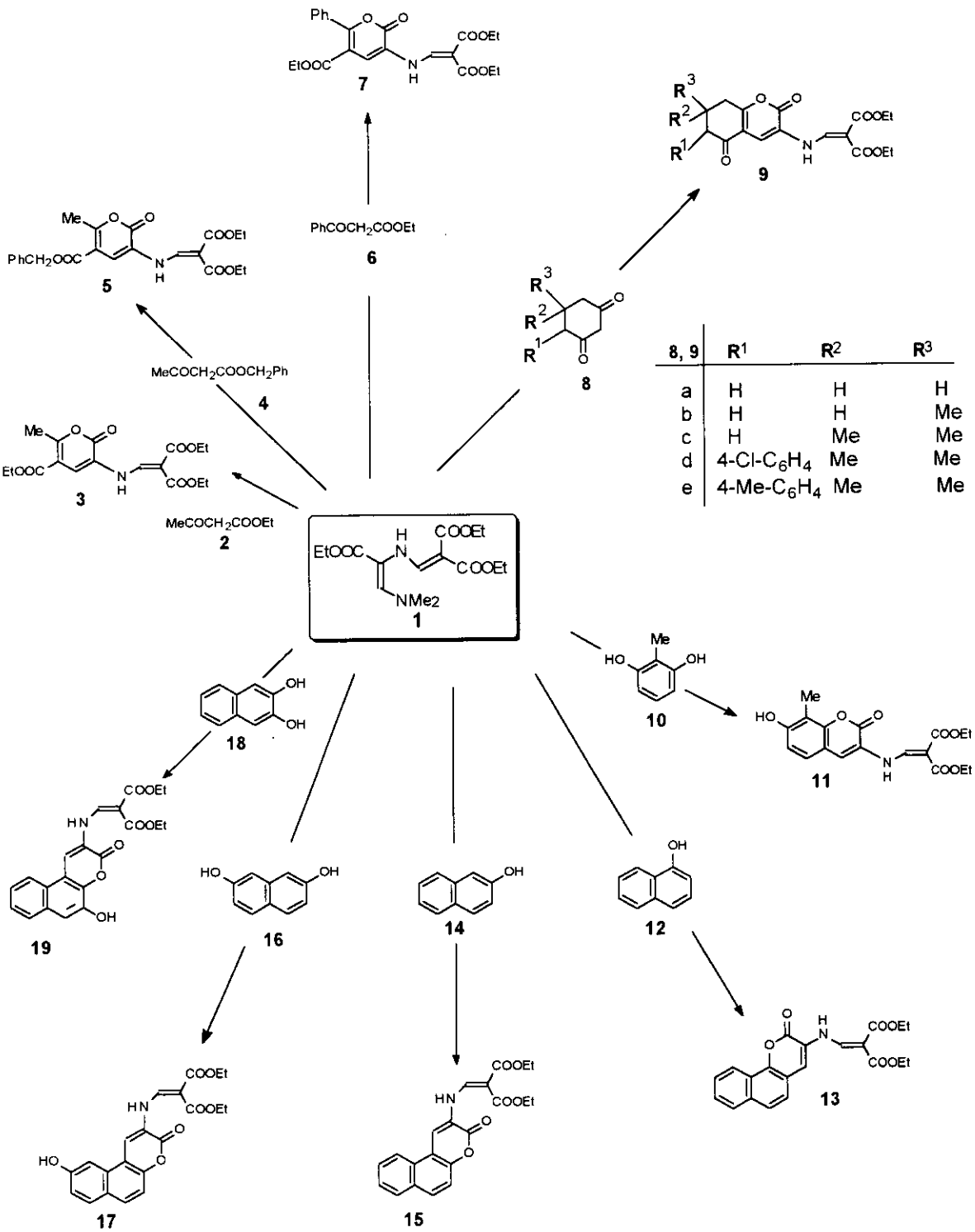
In this paper we report about the application of this reagent (**1**) for the preparation of numerous 2*H*-pyran-2-ones and fused 2*H*-pyran-2-ones by reaction with *C*-nucleophiles, such as β-keto esters, 1,3-diketones, aromatic hydroxy compounds and heterocyclic hydroxy or potentially hydroxy compounds. The reactions were carried out in acetic acid by heating at reflux temperature for several hours. Under these conditions, the dimethylamino group at position 3 of the reagent (**1**) was exchanged with *C*-nucleophiles to form the intermediates, which were further cyclized without isolation. In this manner, β-keto esters (**2**, **4** and **6**) were transformed into 2*H*-pyran-2-one derivatives (**3**, **5** and **7**), 1,3-cyclohexanediones (**8a-e**) into the corresponding 5-oxo-5,6,7,8-tetrahydro-2*H*-1-benzopyran-2-ones (**9a-e**), 2-methylresorcinol (**10**) into 7-hydroxy-2*H*-1-benzopyran-2-one derivative **11**, 1-naphthol (**12**) into 2*H*-naphtho[1,2-*b*]pyran-2-one derivative (**13**), 2-naphthol (**14**), 2,7-dihydroxynaphthalene (**16**), and 2,3-dihydroxynaphthalene (**18**) into the corresponding 3*H*-naphtho[2,1-*b*]pyran-3-one derivatives (**15**, **17**, and **19**), respectively. (Scheme 1).

Heterocyclic hydroxy or potentially hydroxy compounds, such as 4-hydroxy-5-methyl-2*H*-pyran-2-one (**20**) afforded 2*H*,5*H*-pyrano[4,3-*b*]pyran-2-one (**21**), 4-hydroxycoumarin (**22**) was transformed into 2*H*,5*H*-pyrano[3,2-*c*]benzopyran-2,5-dione (**23**), 4-hydroxypyridin-2(1*H*)-one (**24**) into 2*H*-pyrano[3,2-*c*]pyridin-2-one (**25**), 4-hydroxy-1-methylquinolin-2(1*H*)-one (**26**) into 2*H*-pyrano[3,2-*c*]quinolin-2(1*H*)-one (**27**), and 5-hydroxy-6-phenylpyridazin-3(2*H*)-one (**28**) into 2*H*-pyrano[2,3-*d*]pyridazin-2-one derivative (**29**). (Scheme 2).

On the other hand, the heterocyclic compounds with an activated methylene group attached at α-position in respect to the ring nitrogen atom, such as ethyl 2-pyridinylacetate (**30**) and 2-pyridinylacetonitrile (**32**) were converted into 4*H*-quinolizin-4-one derivatives (**31**) and (**33**), respectively. (Scheme 2).

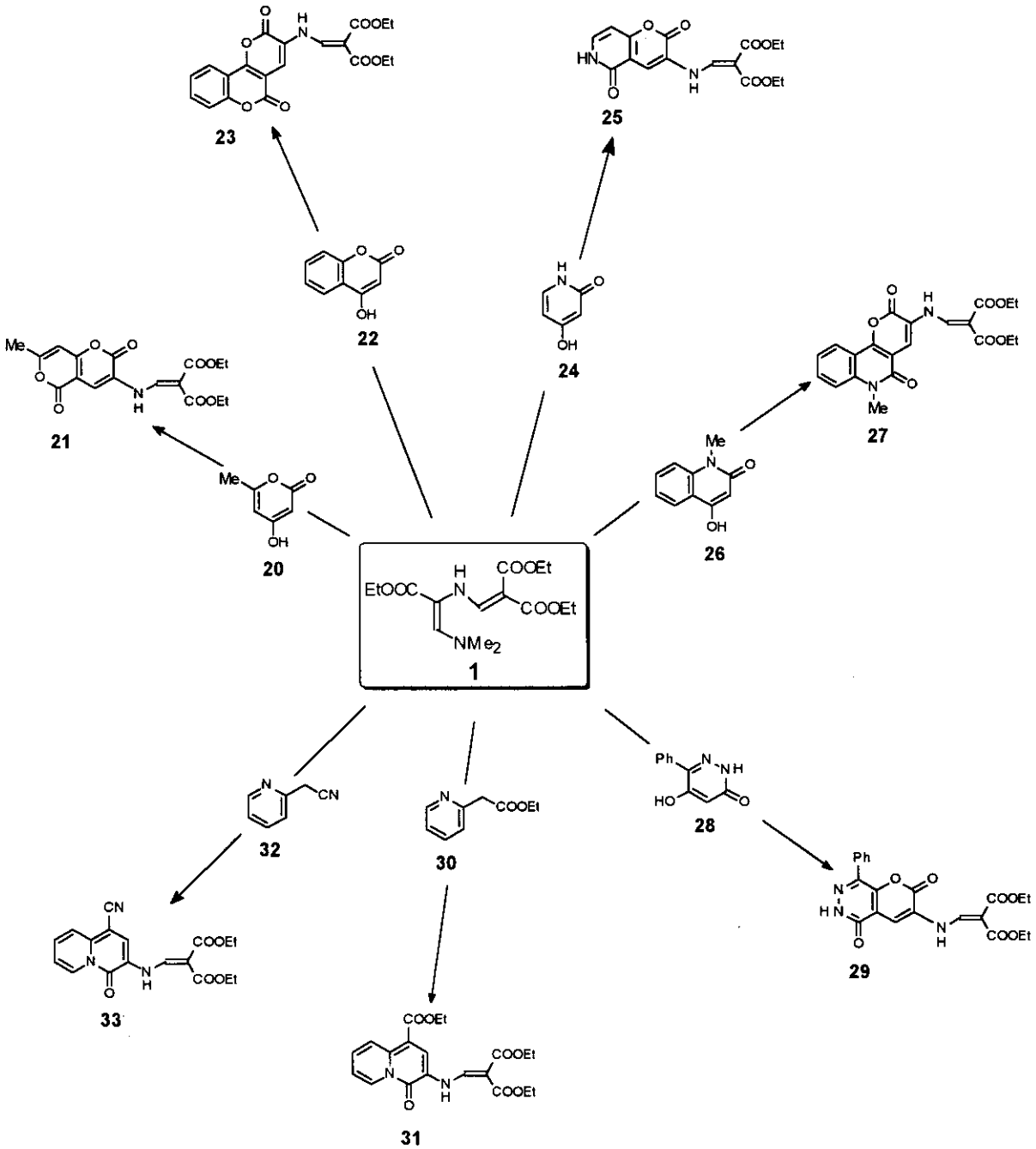
According to this reaction 2,2-bis(ethoxycarbonyl)vinylamino group can be introduced at position 3 in the newly formed heterocyclic systems. The compounds reported in this paper represent intermediates for preparation of 3-amino-2*H*-pyran-2-ones and related systems, and 3-amino-4*H*-quinolizin-4-ones, since 2,2-bis(ethoxycarbonyl)vinyl group can be easily removed from the amino group by treatment with hydrazine. [18,19]

Scheme 1



8, 9	R^1	R^2	R^3
a	H	H	H
b	H	H	Me
c	H	Me	Me
d	4-Cl-C_6H_4	Me	Me
e	4-Me-C_6H_4	Me	Me

Scheme 2



EXPERIMENTAL

Melting points were taken on a Kofler micro hot stage. The ^{1}H NMR spectra were obtained on Varian EM 360 L and Bruker DPX 300 spectrometers, IR spectra on a Perkin-Elmer 1310 instrument, and microanalyses for C, H and N on a Perkin-Elmer Analyser 2400.

Ethyl (*Z*)-2-[2,2-bis(ethoxycarbonyl)vinyl]amino-3-dimethylaminopropenoate (**1**) was prepared according to the procedure we have described previously. [14]

General Procedure. A mixture of the compound with an active methylene group (0.0015 mol) and the compound (**1**) (0.493g, 0.0015 mol) in acetic acid (5 mL) was heated under reflux for several hours. The reaction was followed by tlc (DC-Alufolien Kieselgel 60 F 254, 0.2 mm, E. Merck, and chloroform/methanol, 5:1 and 25:1 as solvent). After the reaction was completed, acetic acid was evaporated *in vacuo* and the solid residue recrystallized from an appropriate solvent to give the product.

3-[2,2-Bis(ethoxycarbonyl)vinyl]amino-5-ethoxycarbonyl-6-methyl-2*H*-pyran-2-one (3). This compound was prepared from **2**, 6 h of reflux, in 6% yield,[20] mp 108-110 °C (ethanol and water); ^{1}H NMR ($CDCl_3$): δ 1.31, 1.37, 1.48 (3t, CH_2CH_3 x 3), 2.67 (s, Het-CH_3), 4.13-4.53 (m, CH_2CH_3 x 3), 7.51 (s, H_4), 8.43 (d, C*H*NH), 10.93 (br d,CHN*H*), $J_{CH_2CH_3}$ = 7.0 Hz, J_{CHNH} = 5.7 Hz. *Anal.* Calcd for $C_{17}H_{21}NO_8$: C, 55.58; H, 5.76; N, 3.81. Found: C, 55.21; H, 5.65; N, 4.01.

3-[2,2-Bis(ethoxycarbonyl)vinyl]amino-5-benzyloxycarbonyl-6-methyl-2*H*-pyran-2-one (5). This compound was prepared from **4**, 6 h of reflux, in 54% yield, mp 98-100 °C (ethanol and water); ^{1}H NMR ($CDCl_3$): δ 1.32, 1.37 (2t, CH_2CH_3 x 2), 2.67 (s, Het-CH_3), 4.32, 4.42 (2q, CH_2CH_3 x 2), 5.42 (s, Ph-CH_2), 7.53-7.62 (m, Ph, H_4), 8.47 (d, C*H*NH), 11.07 (d, CHN*H*), $J_{CH_2CH_3}$ = 7.0 Hz, J_{CHNH} = 14.0 Hz. *Anal.* Calcd for $C_{22}H_{23}NO_8$: C, 61.53; H, 5.40; N, 3.26. Found: C, 61.22; H, 5.16; N, 3.34.

3-[2,2-Bis(ethoxycarbonyl)vinyl]amino-5-ethoxycarbonyl-6-phenyl-2*H*-pyran-2-one (7). This compound was prepared from **6**, 8 h of reflux, in 2% yield,[20] mp 102-104 °C (ethanol and water); ^{1}H NMR ($CDCl_3$): δ 1.09, 1.33, 1.37 (3t, CH_2CH_3 x 3), 4.20, 4.27, 4.36 (3q, CH_2CH_3 x 3), 7.50 (s, H_4),

7.43-7.67 (m, Ph), 8.43 (d, C*H*NH), 9.28 (d, CHN*H*), $J_{CH_2CH_3}$ = 7.0 Hz, J_{CHNH} = 14.0 Hz. *Anal.* Calcd for $C_{22}H_{23}NO_8$: C, 61.53; H, 5.40; N, 3.26. Found: C, 61.25; H, 5.29; N, 3.59.

3-[(2,2-Bis(ethoxycarboyl)vinyl]amino-5-oxo-5,6,7,8-tetrahydro-2*H*-1-benzopyran-2-one (9a). This compound was prepared from **8a**, 2 h of reflux, in 20% yield, mp 115 °C (methanol); ^{1}H NMR (DMSO-d_6): δ 1.22 (t, CH_2CH_3 x 2), 2.50 (d, CH_2), 2.52 (m, CH_2), 2.82 (d, CH_2), 4.22 (q, CH_2CH_3 x 2), 7.68 (s, H_4), 8.46 (d, C*H*NH), 10.68 (d, CHN*H*), J_{CHNH} = 15.0 Hz, $J_{CH_2CH_3}$ = 7.0 Hz, $J_{CH_2CH_2}$ = 6.0 Hz. *Anal.* Calcd for $C_{17}H_{19}NO_7$. MeOH: C, 56.69; H, 6.08; N, 3.67. Found: C, 56.72; H, 5.79; N, 3.59.

3-[(2,2-Bis(ethoxycarboyl)vinyl]amino-7-methyl-5-oxo-5,6,7,8-tetrahydro-2*H*-1-benzopyran-2-one (9b). This compound was prepared from **8b**, 2 h of reflux, in 18% yield, mp 165-166 °C (n-propanol); ^{1}H NMR (DMSO-d_6): δ 1.05 (d, CH*Me*), 1.21 (t, CH_2CH_3 x 2), 2.38, 2.80 (2d, CH_2CHMe x 2), 2.42 (m, C*H*Me), 4.10 (q, CH_2CH_3 x 2), 7.70 (s, H_4), 8.46 (d, C*H*NH), 10.67 (d, CHN*H*), J_{CHNH} = 15.0 Hz, J_{CHCH_2} = 2.0 Hz, $J_{CH_2CH_3}$ = 7.0 Hz, J_{CHCH_3} = 5.0 Hz. *Anal.* Calcd for $C_{18}H_{21}NO_7$: C, 59.50; H, 5.83; N, 3.85. Found: C, 59.40; H, 5.56; N, 3.64.

3-[(2,2-Bis(ethoxycarboyl)vinyl]amino-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-2*H*-1-benzopyran-2-one (9c) This compound was prepared from **8c**, 2 h of reflux, in 50% yield, mp 168-169 °C (ethanol); ^{1}H NMR ($CDCl_3$): δ 1.20 (s, CMe_2), 1.32, 1.36 (2t, CH_2CH_3 x 2), 2.42, 2.76 (2s, CH_2CMe_2 x 2), 4.28, 4.32 (2q, CH_2CH_3 x 2), 7.48 (s, H_4), 8.34 (d, C*H*NH), 10.90 (d, CHN*H*), J_{CHNH} = 15.0 Hz, $J_{CH_2CH_3}$ = 7.0 Hz. *Anal.* Calcd for $C_{19}H_{23}NO_7$: C, 60.45; H, 6.15; N, 3.71. Found: C, 60.34; H, 5.93; N, 3.89.

3-[2,2-Bis(ethoxycarbonyl)vinyl]amino-6-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-2*H*-1-benzopyran-2-one (9d). This compound was prepared from **8d**, 3 h of reflux, in 45% yield, mp 120-123 °C (ethanol); ^{1}H NMR ($CDCl_3$): δ 1.07, 1.17 (2s, CMe_2), 1.34, 1.43 (2t, CH_2CH_3 x 2), 2.80, 2.88 (2d, CH_2CMe_2), 3.58 (s, H_6), 4.31, 4.40 (2q, CH_2CH_3 x 2), 7.13 (d, H_3', H_5') 7.42 (d, H_2', H_4'), 7.57 (s, H_4), 8.43 (d, C*H*NH), 11.12 (d, CHN*H*), $J_{CH_2CH_3}$ = 7.0 Hz, $J_{H_2',H_3'} = J_{H_4',H_5'}$ = 8.0 Hz, Jgem $_{CH_2CMe_2}$ = 18.7 Hz, J_{CHNH} = 14.0 Hz. *Anal.* Calcd for $C_{25}H_{26}NO_7Cl$: C, 61.54; H, 5.37; N, 2.87. Found: C, 61.68; H, 5.09; N, 3.11.

3-[2,2-Bis(ethoxycarbonyl)vinyl]amino-6-(4-methylphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-2*H*-1-benzopyran-2-one (9e). This compound was prepared from **8e**, 3.5 h of reflux, in 33% yield, mp 150-152 °C (ethanol and n-heptane); ^{1}H NMR ($CDCl_3$): δ 0.87, 1.017 (2s, CMe_2), 1.37, 1.417 (2t, CH_2CH_3 x 2), 2.35 (s, Ph-CH_3), 2.48, 2.37 (2d, CH_2CMe_2), 2.83 (s, H_6), 4.15, 4.57 (m, CH_2CH_3 x 2), 7.03 (d, H_3', H_5') 7.27 (d, H_2', H_4'), 7.47 (d, C*H*NH), 7.63 (s, H_4), 8.48 (br s, CHN*H*), $J_{CH_2CH_3}$ = 7.0 Hz, $J_{H_2',H_3'} = J_{H_4',H_5'}$ = 8.0 Hz, Jgem $_{CH_2CMe_2}$ = 18.7 Hz, J_{CHNH} = 14.0 Hz. *Anal.* Calcd for $C_{26}H_{29}NO_7$: C, 66.81; H, 6.25; N, 2.99. Found: C, 66.71; H, 6.16; N, 3.13.

3-[(2,2-Bis(ethoxycarboyl)vinyl]amino-7-hydroxy-8-methyl-2*H*-1-benzopyran-2-one (11). This compound was prepared from **10**, 2h of reflux, in 4% yield,[20] mp 273-275 °C (methanol); ^{1}H NMR (DMSO-d_6): δ 1.22 (t, CH_2CH_3 x 2), 2.14 (s, 8-Me), 4.20 (q, CH_2CH_3 x 2), 6.88 (d, H_5), 7.38 (d, H_6), 8.02 (s, H_4), 8.45 (d, C*H*NH), 10.78 (d, CHN*H*), J_{CHNH} = 15.0 Hz, $J_{CH_2CH_3}$ = 7.0 Hz, J_{H_5,H_6} = 9.0 Hz. *Anal.* Calcd for $C_{18}H_{19}NO_7$: C, 59.83; H, 5.30; N, 3.88. Found: C, 59.61; H, 5.50; N, 3.88.

3-[2,2-Bis(ethoxycarbonyl)vinyl]amino-2*H*-naphtho[1,2-*b*]pyran-2-one (13). This compound was prepared from **12**, 5 h of reflux, in 35% yield, mp 204-206 °C (ethanol); ^{1}H NMR (DMSO-d_6): δ 1.30 (t, CH_2CH_3 x 2), 4.25, 4.33 (2q, CH_2CH_3 x 2), 7.70-8.77 (m, H_5, H_6, H_7, H_8, H_9, H_{10}, C*H*NH), 8.26 (s, H_4), 10.90 (br s, CHN*H*), $J_{CH_2CH_3}$ = 7.0 Hz. *Anal.* Calcd for $C_{21}H_{19}NO_6$: C, 66.14; H, 5.02; N, 3.67. Found: C, 66.12; H, 4.92; N, 3.71.

2-[2,2-Bis(ethoxycarbonyl)vinyl]amino-3*H*-naphtho[2,1-*b*]pyran-3-one (15). This compound was prepared from **14**, 8 h of reflux, in 40% yield, mp 179-182 °C (ethanol and ethyl acetate); ^{1}H NMR ($CDCl_3$): δ 1.26, 1.32 (2t, CH_2CH_3 x 2), 4.62, 4.84 (2q, CH_2CH_3 x 2), 7.46 (d, H_6), 7.60 (ddd, H_9), 7.72 (ddd, H_8), 7.60 (d, H_5), 7.69 (d, H_7), 8.07 (s, H_1), 8.28 (d, H_{10}), 8.73 (d, C*H*NH), 11.35 (d, CHN*H*), $J_{CH_2CH_3}$ = 7.1 Hz, J_{H_5,H_6} = 9.0 Hz, J_{H_7,H_8} = 7.7 Hz, $J_{H_8,H_9} = J_{H_9,H_{10}}$ = 8.4 Hz, J_{CHNH} = 13.6 Hz. *Anal.* Calcd for $C_{21}H_{19}NO_6$: C, 66.14; H, 5.02; N, 3.67. Found: C, 65.97; H, 4.90; N, 3.69.

2-[2,2-Bis(ethoxycarbonyl)vinyl]amino-9-hydroxy-3*H*-naphtho[2,1-*b*]pyran-3-one (17). This compound was prepared from **16**, 6 h of reflux, in 65% yield, mp 241-243 °C (ethanol and ethyl

acetate); ^{1}H NMR (DMSO-d_6): δ 1.30 (t, CH_2CH_3 x 2), 4.30, 4.33 (2q, CH_2CH_3 x 2), 7.30 (d, H_7), 7.43 (d, H_6), 7.90 (d, H_5), 8.07 (d, H_9), 8.11 (d, H_4), 8.76 (s, H_1), 8.95 (d, CHNH), 10.26 (br s, OH), 11.12 (d, CHNH), $J_{CH_2CH_3}$ = 7.1 Hz, J_{H_4,H_5} = 9.2 Hz, J_{H_6,H_7} = 9.0 Hz, J_{H_7,H_9} = 8.4 Hz, J_{CHNH} = 14.0 Hz. *Anal.* Calcd for $C_{21}H_{19}NO_7$: C, 63.47; H, 4.82; N, 3.52. Found: C, 63.08; H, 4.65; N, 3.73.

2-[2,2-Bis(ethoxycarbonyl)vinyl]amino-5-hydroxy-3*H*-naphtho[2,1-*b*]pyran-3-one (19). This compound was prepared from **18**, 0.5 h of reflux, in 45% yield, mp 223-226 °C (ethanol); ^{1}H NMR (DMSO-d_6): δ 1.29, 1.29 (2t, CH_2CH_3 x 2), 4.22, 4.25 (2q, CH_2CH_3 x 2), 7.39 (s, H_6), 7.51 (2ddd, H_8, H_9), 7.87 (dd, H_7), 8.64 (dd, H_{10}), 8.82 (d, CHNH), 8.82 (s, H_1), 10.59 (br s, OH), 11.00 (d, CHNH), $J_{CH_2CH_3}$ = 7.1 Hz, J_{H_7,H_8} = J_{H_8,H_9} = $J_{H_9,H_{10}}$ = 9.5 Hz, J_{H_7,H_9} = $J_{H_8,H_{10}}$ = 3.2 Hz, J_{CHNH} = 13.6 Hz. *Anal.* Calcd for $C_{21}H_{19}NO_7$: C, 63.47; H, 4.82; N, 3.52. Found: C, 63.12; H, 4.63; N, 3.52.

3-[2,2-Bis(ethoxycarbonyl)vinyl]amino-7-methyl-5-oxo-2*H*,5*H*-pyrano[4,3-*b*]pyran-2-one (21). This compound was prepared from **20**, 0.5 h of reflux, in 65% yield, mp 182-183 °C (ethanol); ^{1}H NMR ($CDCl_3$): δ 1.33, 1.37 (2t, CH_2CH_3 x 2), 2.37 (s, 7-Me), 4.33, 4.38 (2q, CH_2CH_3 x 2), 6.42 (s, H_8), 7.53 (s, H_4), 8.37 (d, CHNH), NH-exchanged, $J_{CH_2CH_3}$ = 8.0 Hz, J_{CHNH} = 13.0 Hz. *Anal.* Calcd for $C_{17}H_{17}NO_8$: C, 56.20; H, 4.72; N, 3.86. Found: C, 55.85; H, 4.65; N, 3.98.

3-[2,2-Bis(ethoxycarbonyl)vinyl]amino-5-oxo-2*H*,5*H*-pyrano[3,2-*c*]benzopyran-2-one (23). This compound was prepared from **22**, 1 h of reflux, in 41% yield, mp 201-203 °C (ethanol); ^{1}H NMR ($CDCl_3$): δ 1.27, 1.33 (2t, CH_2CH_3 x 2), 4.27, 4.38 (2q, CH_2CH_3 x 2), 7.33-8.12 (m, H_7, H_8, H_9, H_{10},) 7.61 (s, H_4), 8.33 (d, CHNH), 11.01 (d, CHNH), $J_{CH_2CH_3}$ = 7.0 Hz, J_{CHNH} = 13.0 Hz. *Anal.* Calcd for $C_{20}H_{17}NO_8$: C, 60.15; H, 4.29; N, 3.50. Found: C, 60.31; H, 4.14; N, 3.65.

3-[2,2-Bis(ethoxycarbonyl)vinyl]amino-5-oxo-5,6-dihydro-2*H*-pyrano[3,2-*c*]pyridin-2-one (25). This compound was prepared from **24**, 2 h of reflux, in 25% yield, mp 271-273 °C (*N*,*N*-dimethylformamide and water); ^{1}H NMR (DMSO-d_6): δ 1.36, 1.38 (2t, CH_2CH_3 x 2), 4.30, 4.35 (2q, CH_2CH_3 x 2), 6.42 (d, H_7), 7.38 (d, H_8), 7.81 (s, H_4), 8.48 (d, CHNH), 11.08 (d, CHNH), $J_{CH_2CH_3}$ =

7.2 Hz, J_{H_7,H_8} = 7.3 Hz, J_{CHNH} = 13.5 Hz. *Anal.* Calcd for $C_{16}H_{16}N_2O_7$: C, 55.17; H, 4.63; N, 8.04. Found: C, 54.93; H, 4.56; N, 8.08.

3-[2,2-Bis(ethoxycarbonyl)vinyl]amino-6-methyl-5-oxo-5,6-dihydro-2*H*-pyrano[3,2-*c*]quinolin-2-one (27). This compound was prepared from **26**, 10 min of reflux, in 65% yield, mp 195-196 °C (ethanol); ^{1}H NMR ($CDCl_3$): δ 1.37, 1.43 (2t, CH_2CH_3 x 2), 3.80 (s, 6-Me), 4.04, 4.43 (2q, CH_2CH_3 x 2), 7.28-8.37 (m, H_7, H_8, H_9, H_{10}), 7.90 (s, H_4), 8.53 (d, CHNH), 11.23 (d, CHNH), $J_{CH_2CH_3}$ = 8.0 Hz, J_{CHNH} = 13.0 Hz. *Anal.* Calcd for $C_{21}H_{20}N_2O_7$: C, 61.16; H, 4.89; N, 6.79. Found: C, 61.06; H, 4.75; N, 6.79.

3-[2,2-Bis(ethoxycarbonyl)vinyl]amino-8-phenyl-5-oxo-5,6-dihydro-2*H*-pyrano[2,3-*d*]pyridazin-2-one (29). This compound was prepared from **28**, 2.5 h of reflux, in 52% yield, mp 273-275 °C (ethanol); ^{1}H NMR (CF_3COOD): δ 1.00, 1.08 (2t, CH_2CH_3 x 2), 4.07, 4.08 (2q, CH_2CH_3 x 2), 7.10-7.51 (m, Ph), 7.83 (s, H_4), 8.50 (d, CHNH), H_6, NHCH - exchanged, $J_{CH_2CH_3}$ = 7.0 Hz. *Anal.* Calcd for $C_{21}H_{19}N_3O_7$: C, 59.29; H, 4.50; N, 9.88. Found: C, 58.58; H, 4.41; N, 9.71.

3-[2,2-Bis(ethoxycarbonyl)vinyl]amino-1-ethoxycarbonyl-4*H*-quinolizin-4-one (31). This compound was prepared from **30**, 6 h of reflux, in 10% yield, mp 176-178 °C (ethanol); ^{1}H NMR ($CDCl_3$): δ 1.38, 1.40, 1.42 (3t, CH_2CH_3 x 3), 4.30, 4.37, 4.45 (3q, CH_2CH_3 x 3), 7.29 (ddd, H_7), 7.56 (ddd, H_8), 8.40 (s, H_2), 8.72 (d, CHNH), 9.26 (2dd, H_6, H_9), 11.31 (br d,CHNH), $J_{CH_2CH_3}$ = 7.0 Hz, J_{CHNH} = 14.0 Hz, J_{H_6,H_7} = J_{H_8,H_9} = 8.0 Hz, J_{H_6,H_8} = J_{H_7,H_9} = 2.0 Hz. *Anal.* Calcd for $C_{20}H_{22}N_2O_7$: C, 59.70; H, 5.51; N, 6.96. Found: C, 59.64; H, 5.61; N, 6.96.

3-[2,2-Bis(ethoxycarbonyl)vinyl]amino-1-cyano-4*H*-quinolizin-4-one (33). This compound was prepared from **32**, 2 h of reflux, in 61% yield, mp 213-215 °C (ethanol and toluene); ^{1}H NMR ($CDCl_3$): δ 1.38, 1.40 (2t, CH_2CH_3 x 2), 4.30, 4.40 (2q, CH_2CH_3 x 2), 7.34 (ddd, H_7),7.57 (ddd, H_8), 7.79 (s, H_2), 8.04 (dd,H_9), 8.51 (d, CHNH), 9.21 (dd, H_6), 11.38 (br d,CHNH), $J_{CH_2CH_3}$ = 7.5 Hz, J_{CHNH} = 14.0 Hz, J_{H_6,H_7} = 7.0 Hz, J_{H_8,H_9} = 8.0 Hz, J_{H_6,H_8} = J_{H_7,H_9} = 2.0 Hz. *Anal.* Calcd for $C_{18}H_{17}N_3O_5$: C, 60.84; H, 4.82; N, 11.83. Found: C, 60.73; H, 4.76; N, 11.97.

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REFERENCES AND NOTES

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