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Indoline-2-thiones **1a-b,d,f,h**, which have at least one hydrogen at the 3-position reacted with α -halo ester **2a-d**, α -halo ketones **2e-f**, and α -bromoacetonitrile **2g** to give 2-alkylthioindole derivatives **3-11**. In a similar manner treatment of 3,3-disubstituted indoline-2-thiones **1c,e** with α -halo esters **2a,c,d** and α -halo ketone **2e** gave 2-alkylthioindolenines **12-16**. Treatment of 1,3,3-trisubstituted indoline-2-thiones **1g,i** with ethyl bromoacetate **2a** resulted in recovery of starting materials. Desulfurization of indolenine **14** with triphenylphosphine gave 2-alkylideneindoline **19**.

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Indoline-2-thiones, which are easily accessible by direct sulfuration of their oxygen analogues with dimer of *p*-methoxyphenylthionophosphine (Lawesson's reagent), are useful synthetic intermediates for the synthesis of indole derivatives [1]. In addition 2-alkylideneindolines are regarded as important starting materials for the synthesis of photochromic compounds, spiropyrans [2]. The Eschenmoser condensation-extrusion reaction is an efficient method for the C-C bond formation [3-4]. In this paper, we describe the results of direct condensation of indoline-2-thiones **1** with α -activated esters **2a-d** and ketones **2e-f** yielding the indole **3-11** and indolenine derivatives **12-16**.

Indoline-2-thiones **1a-b,d,f,h**, which have at least one hydrogen at 3-position, were treated with α -activated esters such as ethyl bromoacetate **2a**, ethyl chloroacetate **2b**, ethyl 2-bromobutanoate **2c** and methyl bromoacetate **2d** in the presence of triphenylphosphine, triethylamine and sodium iodide to yield 2-(alkoxycarbonylalkylthio)indole derivatives

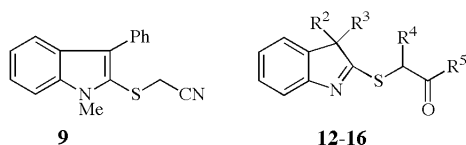
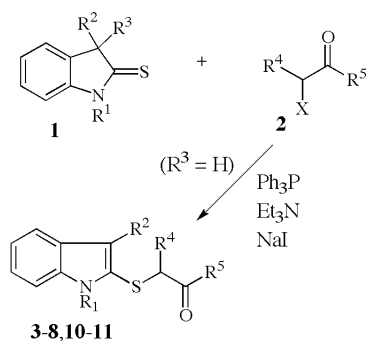
3,5,7,10-11. Treatment of indoline-2-thione **1f** with ethyl bromoacetate **2a** in the absence of triphenylphosphine under the same conditions also gave indole derivative **7**, but in low yield. In a similar manner indoline-2-thiones **1b,d,f** reacted smoothly with α -bromoketones **2e-f** and bromoacetonitrile **2g** to give the corresponding 2-substituted indole derivatives **4,6,8-9**. Reductive product, propiophenone was formed by the reaction of **1b** and α -bromopropiophenone **2e**. The structures of **3-11** were elucidated on the basis of spectroscopic properties and microanalyses, the latter indicating that they were the dehydrohalogenation products of 1:1 adduct of indoline-2-thiones **1** and **2**. Treatment of 1-methyl-2-(ethoxycarbonylmethylthio)-3-phenylindoline **7** with equimolar amount of *m*-chloroperbenzoic acid (MCPBA) gave the corresponding sulfoxide **17** in 59% yield, exclusively, while treatment of **7** with 2 molar equivalent of MCPBA gave the corresponding sulfoxide **17** and sulfone **18** in 16 and 17% yields, respectively, along with

Table
Yields of Indole **3-11** and Indolenine Derivatives **12-16**.

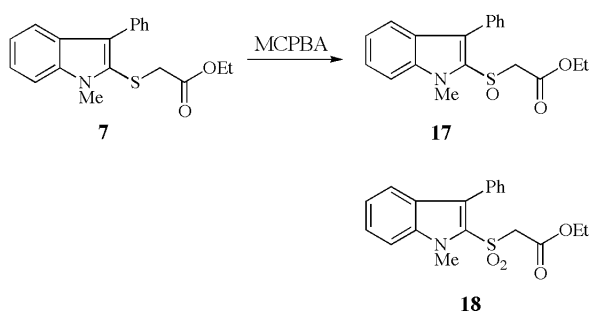
	Thione 1				Halide 2			Yield (%) [a] of 3-16
	R ¹	R ²	R ³		R ⁴	R ⁵	X	
1a	H	H	H	2a	H	EtO	Br	3 (46)
1b	H	Me	H	2e	Me	Ph	Br	4 (45) propiophenone (50)
1c	H	Me	Me	2a	H	EtO	Br	12 (84)
1c	H	Me	Me	2d	H	MeO	Br	13 (72)
1d	H	Ph	H	2d	H	MeO	Br	5 (23)
1d	H	Ph	H	2f	H	Ph	Br	6 (29)
1e	H	Ph	Ph	2a	H	EtO	Br	14 (46)
1e	H	Ph	Ph	2c	Et	EtO	Br	15 (44)
1e	H	Ph	Ph	2e	Me	Ph	Br	16 (66) propiophenone (31)
1f	Me	Ph	H	2a	H	EtO	Br	7 (93)
1f[b]	Me	Ph	H	2a	H	EtO	Br	7 (19)
1f	Me	Ph	H	2b	H	EtO	Cl	7 (75)
1f	Me	Ph	H	2f	H	Ph	Br	8 (95)
1f	Me	Ph	H	2g		BrCH ₂ CN		9 (75)
1g	Me	Me	Me	2a	H	EtO	Br	no reaction
1h	Ph	H	H	2a	H	EtO	Br	10 (30)
1h	Ph	H	H	2c	Et	EtO	Br	11 (76)
1i	Ph	Me	Me	2a	H	EtO	Br	no reaction

[a] Isolated yield; [b] In the absence of Ph₃P.

Scheme 1

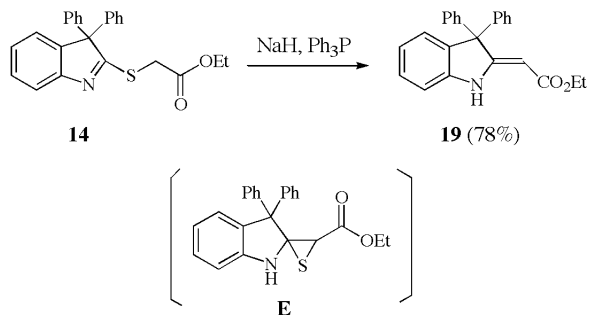


Scheme 2



several small amounts of unidentified products. Attempts for the sulfur extrusion of 2-(ethoxycarbonylmethylthio)indole **7** were unsuccessful. Treatment of **7** with base such as triethylamine and sodium hydride, and triphenylphosphine resulted in recovery of unchanged **7**. On the other hand, treatment of 3,3-disubstituted indoline-2-thiones **1c,e** possessing no hydrogen at the 3-position with α -halo

Scheme 3



esters **2a, c-d** and α -bromopropiophenone **2e** under similar conditions yielded indolenine derivatives **12-16**. Treatment of 2-(ethoxycarbonylmethylthio)-3,3-diphenylindolenine **14** thus obtained with sodium hydride and triphenylphosphine gave the corresponding 2-alkylideneindolenine **19** in good yield. The mechanism for the formation of **19** can be explained in terms of episulfide intermediate **E** [3]. When 1,3,3-trisubstituted indoline-2-thiones **1g,i** were treated with ethyl bromoacetate **2a** under the same conditions, the unchanged starting materials were recovered quantitatively.

EXPERIMENTAL

Melting and boiling points were measured with Yanaco micro melting point apparatus (MP-3J) and Sibata glass tube oven distillation apparatus (GOT-350RD) respectively and are uncorrected. The ir spectra were recorded on JASCO FT/IR-300 spectrophotometer (in cm^{-1}). The ^1H and ^{13}C nmr spectra were run on JEOL JMN-EX 270 (270 MHz) and Varian GEMINI 200 (200 MHz) spectrometers in deuteriumchloroform using TMS as an internal standard (δ in ppm, J in Hz). Chromatographic purifications were carried out on a silica gel column (flash chromatography: Wakogel C-300).

Reaction of Indoline-2-thiones **1** with α -Halo Esters **2a-d**, α -Bromopropiophenone **2e**, α -Bromoacetophenone **2f**, or Bromoacetonitrile **2g**.

Typical procedure: To a solution of indoline-2-thione **1** (1 mmol), the corresponding halide **2** (1 mmol), and sodium iodide (2 mmol) in acetonitrile (50 ml) under argon was added dropwise a solution of triphenylphosphine (2 mmol) and triethylamine (2 mmol) in acetonitrile (20 ml) at reflux temperature. The mixture was refluxed for 4-10 hours, and then poured into water and extracted with ethyl acetate. The organic layer was washed with dilute hydrochloric acid (HCl), sodium bicarbonate (NaHCO_3) solution, and H_2O and dried over anhydrous magnesium sulfate (MgSO_4). After removal of the solvent, the residue was chromatographed on a silica gel column with toluene-hexane (4:1-1:1) to give indole or indolenine derivatives **3-16**.

2-Ethoxycarbonylmethylthioindole (3).

This compound had mp 42-43°; ir: ν (KBr) 3388, 1726, 1296, 1181; ^1H nmr: δ 1.26 (t, 3H, $J=7.2$), 3.51 (s, 2H), 4.21 (q, 2H, $J=7.2$), 6.67 (s, 1H), 7.05-7.57 (m, 4H), 9.12 (br s, 1H); ^{13}C nmr: δ 13.6, 38.0, 61.7, 108.5, 110.5, 119.7, 120.0, 122.5, 126.9, 127.7, 137.1, 171.3.

Anal. Calcd. for $\text{C}_{12}\text{H}_{13}\text{NO}_2\text{S}$ (233.2): C, 61.27; H, 5.57; N, 5.96. Found: C, 61.07; H, 5.51; N, 5.75.

2-(1-Benzoylthio)-3-methylindole (4).

This compound had mp 44-45°; ir: ν (KBr) 3374, 1680; ^1H nmr: δ 1.47 (d, 3H, $J=7.0$), 2.27 (s, 3H), 4.55 (q, 1H, $J=7.0$), 7.04-7.59 (m, 8H), 7.89-7.95 (m, 1H), 8.14 (br s, 1H); ^{13}C nmr: δ 9.1, 16.4, 45.7, 110.4, 119.0, 120.4, 123.0, 128.3, 133.0, 135.7, 197.5.

Anal. Calcd. for $\text{C}_{18}\text{H}_{17}\text{NOS}$ (295.3): C, 73.20; H, 5.80; N, 4.74. Found: C, 73.30; H, 5.85; N, 4.61.

2-Methoxycarbonylmethylthio-3-phenylindole (**5**).

This compound had mp 167-169°; ir: ν (KBr) 1725, 1306, 1257, 1159, 1140; ^1H nmr: δ 2.16 (s, 3H), 4.25 (s, 2H), 7.23-7.77 (m, 8H), 8.14-8.19 (m, 1H); ^{13}C nmr: δ 30.3, 37.6, 112.9, 118.3, 123.0, 124.6, 126.6, 126.9, 128.0, 128.2, 128.7, 131.2, 132.0, 172.7

Anal. Calcd. for $\text{C}_{17}\text{H}_{15}\text{NO}_2\text{S}$ (297.3): C, 68.67; H, 5.06; N, 4.71. Found: C, 68.77; H, 5.31; N, 5.02.

2-Benzoylmethylthio-3-phenylindole (**6**).

This compound had mp 116-117°; ir: ν (KBr) 3369, 1673, 749, 699; ^1H nmr: δ 4.07 (s, 2H), 7.07-7.96 (m, 14H), 9.15 (br s, 1H); ^{13}C nmr: δ 41.8, 110.6, 119.3, 120.0, 122.0, 123.0, 125.6, 126.3, 127.1, 128.0, 128.2, 128.4, 129.6, 133.6, 134.9, 135.8, 196.1.

Anal. Calcd. for $\text{C}_{22}\text{H}_{17}\text{NOS}$ (343.4): C, 76.93; H, 4.99; N, 4.08. Found: C, 76.69; H, 5.07; N, 4.07.

2-Ethoxycarbonylmethylthio-*N*-methyl-3-phenylindole (**7**).

This compound had bp 250° at 2 Torr; ir: ν (film) 1731, 1370, 1323, 1268, 1126; ^1H nmr: δ 1.14 (t, 3H, $J = 7.2$), 3.34 (s, 2H), 4.00 (s, 3H), 4.01 (q, 2H, $J = 7.2$), 7.19-7.83 (m, 9H); ^{13}C nmr: δ 13.3, 29.7, 38.0, 60.9, 109.3, 119.5, 119.7, 123.6, 124.8, 126.1, 127.8, 128.7, 129.6, 133.5, 137.4, 168.5.

Anal. Calcd. for $\text{C}_{19}\text{H}_{19}\text{NO}_2\text{S}$ (325.3): C, 70.10; H, 5.89; N, 4.31. Found: C, 69.95; H, 5.98; N, 4.01.

2-Benzoylmethylthio-*N*-methyl-3-phenylindole (**8**).

This compound had mp 112-113°; ir: ν (KBr) 1684, 751, 701; ^1H nmr: δ 3.93 (s, 3H), 3.92 (s, 2H), 7.18-7.80 (m, 14H); ^{13}C nmr: δ 29.7, 42.0, 109.5, 119.6, 119.9, 123.2, 123.3, 126.3, 128.0, 128.1, 128.2, 129.8, 133.0, 134.4, 134.8, 137.3, 193.8.

Anal. Calcd. for $\text{C}_{23}\text{H}_{19}\text{NOS}$ (357.4): C, 77.28; H, 5.36; N, 3.92. Found: C, 76.91; H, 5.50; N, 3.74.

2-Cyanomethylthio-*N*-methyl-3-phenylindole (**9**).

This compound had bp 235° at 2 Torr; ir: ν (film) 2230, 1600, 1460, 744, 699; ^1H nmr: 2.91 δ (s, 2H), 3.78 (s, 3H), 6.95-7.56 (m, 9H); ^{13}C nmr: δ 21.7, 30.2, 109.9, 120.0, 120.3, 124.0, 125.8, 126.8, 128.2, 128.5, 129.9, 132.9, 137.4.

Anal. Calcd. for $\text{C}_{17}\text{H}_{14}\text{N}_2\text{S}$ (278.3): C, 73.36; H, 5.07; N, 10.07. Found: C, 73.47; H, 5.23; N, 10.37.

2-Ethoxycarbonylmethylthio-*N*-phenylindole (**10**).

This compound had mp 34°; ir: ν (KBr) 1739, 1286, 1183, 1149, 1105; ^1H nmr: δ 1.12 (t, 3H, $J = 7.2$), 3.25 (s, 2H), 4.04 (q, 2H, $J = 7.2$), 6.84 (s, 1H), 7.10-7.78 (m, 9H); ^{13}C nmr: δ 13.5, 37.2, 61.1, 109.5, 110.1, 119.9, 120.2, 122.6, 127.8, 128.1, 128.3, 129.0, 131.8, 132.0, 138.7, 169.0.

Anal. Calcd. for $\text{C}_{18}\text{H}_{17}\text{NO}_2\text{S}$ (311.3): C, 69.44; H, 5.50; N, 4.50. Found: C, 69.50; H, 5.31; N, 4.45.

2-(1-Ethoxycarbonylpropylthio)-*N*-phenylindole (**11**).

This compound had bp 215° at 2 Torr; ir: ν (film) 1731, 1312, 1296, 1213, 1156; ^1H nmr: δ 0.77 (t, 3H, $J = 7.4$), 1.03 (t, 3H, $J = 7.1$), 1.45-1.80 (m, 2H), 3.14 (t, 1H, $J = 7.4$), 3.96 (q, 2H, $J = 7.1$), 6.88 (s, 1H), 7.06-7.61 (m, 9H); ^{13}C nmr: δ 11.1, 13.5, 24.1, 52.6, 60.6, 110.3, 111.8, 120.1, 120.2, 122.9, 126.8, 127.1, 128.4, 128.8, 136.8, 138.8, 171.2.

Anal. Calcd. for $\text{C}_{20}\text{H}_{21}\text{NO}_2\text{S}$ (339.4): C, 70.71; H, 6.24; N, 4.13. Found: C, 70.89; H, 6.33; N, 4.14.

2-Ethoxycarbonylmethylthio-3,3-dimethylindolenine (**12**).

This compound had bp 185° at 2 Torr; ir: ν (film) 1737, 1619, 1298, 1209, 1090; ^1H nmr: δ 1.30 (t, 3H, $J = 8.3$), 1.38 (s, 6H), 4.13 (s, 2H), 4.21 (q, 2H, $J = 8.3$), 7.02-7.48 (m, 4H); ^{13}C nmr: δ 13.5, 24.5, 32.3, 54.6, 61.3, 118.2, 120.4, 123.3, 127.2, 145.2, 152.8, 168.3, 186.1; Ms: m/z 263 (M^+), 176.

Anal. Calcd. for $\text{C}_{14}\text{H}_{17}\text{NO}_2\text{S}$ (263.3): C, 63.86; H, 6.51; N, 5.32. Found: C, 63.81; H, 6.60; N, 5.65.

2-Methoxycarbonylmethylthio-3,3-dimethylindolenine (**13**).

This compound had mp 136-137°; ir: ν (KBr) 1713, 1675, 1338, 1225, 1212; ^1H nmr: δ 1.38 (s, 6H), 3.78 (s, 3H), 4.18 (s, 2H), 7.10-7.50 (m, 4H); ^{13}C nmr: δ 24.5, 32.0, 52.3, 54.4, 118.5, 120.6, 124.0, 124.4, 145.6, 152.7, 169.0, 186.0.

Anal. Calcd. for $\text{C}_{13}\text{H}_{15}\text{NO}_2\text{S}$ (249.3): C, 62.64; H, 6.07; N, 5.62. Found: C, 62.83; H, 5.85; N, 5.31.

2-Ethoxycarbonylmethylthio-3,3-diphenylindolenine (**14**).

This compound had mp 132-133°; ir: ν (KBr) 1744, 1301, 1167, 1121; ^1H nmr: δ 1.28 (t, 3H, $J = 7.3$), 4.03 (s, 2H), 4.23 (q, 2H, $J = 7.3$), 7.07-7.52 (m, 14H); ^{13}C nmr: δ 14.1, 33.7, 61.7, 73.0, 119.4, 124.1, 125.0, 127.5, 128.2, 128.3, 128.6, 128.7, 131.9, 141.2, 144.9, 153.8, 168.6, 183.7.

Anal. Calcd. for $\text{C}_{24}\text{H}_{21}\text{NO}_2\text{S}$ (387.4): C, 74.39; H, 5.46; N, 3.62. Found: C, 74.58; H, 5.60; N, 3.33.

2-(1-Ethoxycarbonylpropylthio)-3,3-diphenylindolenine (**15**).

This compound had bp 240° at 2 Torr; ir: ν (film) 1731, 1302, 1258, 1158, 1119; ^1H nmr: δ 0.99 (t, 3H, $J = 7.4$), 1.24 (t, 3H, $J = 7.2$), 1.85-2.05 (m, 2H), 4.23 (q, 2H, $J = 7.4$), 4.61 (t, 1H, $J = 7.2$), 7.03-7.52 (m, 14H); ^{13}C nmr: δ 11.1, 13.7, 24.7, 49.4, 61.0, 72.8, 119.0, 123.8, 124.6, 125.0, 127.1, 127.3, 128.2, 128.7, 137.5, 140.7, 141.1, 144.6, 158.3, 171.4, 183.5.

Anal. Calcd. for $\text{C}_{26}\text{H}_{25}\text{NO}_2\text{S}$ (415.5): C, 75.16; H, 6.07; N, 3.37. Found: C, 75.01; H, 6.07; N, 3.44.

2-(1-Benzoylthio)-3,3-diphenylindolenine (**16**).

This compound had mp 136-138°; ir: ν (KBr) 1679, 1592, 1503, 765, 748, 698; ^1H nmr: δ 1.61 (d, 3H, $J = 7.2$), 5.77 (q, 1H, $J = 7.2$), 7.08-8.08 (m, 19H); ^{13}C nmr: δ 17.2, 44.7, 73.9, 119.3, 124.5, 125.4, 127.7, 127.8, 128.1, 128.2, 128.4, 128.5, 131.9, 133.0, 133.6, 135.6, 137.0, 141.0, 141.6, 154.2, 197.8.

Anal. Calcd. for $\text{C}_{29}\text{H}_{23}\text{NOS}$ (433.5): C, 80.35; H, 5.35; N, 3.23. Found: C, 80.04; H, 5.45; N, 3.07.

Oxidation of 2-Ethoxycarbonylmethylthio-*N*-methyl-3-phenylindole **7** with *m*-Chloroperbenzoic Acid (MCPBA).

To a solution of 2-ethoxycarbonylmethylthio-*N*-methyl-3-phenylindole **7** (1 mmol) in dichloromethane (30 ml) was added dropwise a solution of MCPBA (1-2 mmol) in dichloromethane (20 ml) at 0° (ice-bath) under argon and then the mixture was stirred for 2-4 hours at room temperature. The reaction mixture was poured into water and extracted with dichloromethane. Organic layer was washed with dilute HCl, NaHCO_3 solution, water, and then dried over anhydrous MgSO_4 . After removal of the solvent, the residue was chromatographed with toluene-hexane (4:1) to give the corresponding sulfinyl **17** and sulfonyl compounds **18**.

2-Ethoxycarbonylmethylsulfonyl-*N*-methyl-3-phenylindole (**17**).

This compound had bp 250° at 2 Torr (dec.); ir: ν (film) 1730, 1333, 1265, 1099, 1049; ^1H nmr: δ 1.01 (t, 3H, $J = 7.2$), 3.99 (q, 2H, $J = 7.2$), 4.02 (d, 1H, $J = 13.2$), 4.21 (s, 3H), 4.32 (d, 1H, $J = 13.2$), 7.11-7.27 (m, 1H), 7.34-7.51 (m, 7H), 7.67 (d, 1H, $J = 8.3$); ^{13}C nmr: δ 13.6, 31.3, 58.0, 62.1, 109.5, 121.0, 121.3, 125.3, 125.6, 127.5, 128.4, 129.3, 130.5, 131.7, 139.3, 163.4; Ms: m/z 341 (M^+), 325, 254. The result of elemental analysis of this compound was not in accord with the calculated values since **17** decomposed on distillation.

2-Ethoxycarbonylmethylsulfonyl-*N*-methyl-3-phenylindole (**18**).

Compound **18** as obtained as a viscous oil; ir: ν (film) 1729, 1367, 1339, 1262, 1207, 1146; ^1H nmr: δ 1.02 (t, 3H, $J = 7.1$), 3.92 (s, 3H), 4.02 (q, 2H, $J = 7.1$), 4.13 (s, 2H), 7.13-7.52 (m, 9H), 7.89-8.04 (m, 2H); ^{13}C nmr: δ 13.2, 31.6, 52.0, 61.5, 109.9, 121.1, 126.3, 127.3, 127.6, 127.7, 129.3, 130.7, 132.6, 137.5, 139.0, 161.9; Ms: m/z 357 (M^+), 325, 238.

Reaction of 2-Ethoxycarbonylmethylthio-3,3-diphenylindolenine **14** with Sodium Hydride and Triphenylphosphine.

To a solution of 2-ethoxycarbonylmethylthio-3,3-diphenylindolenine **14** (1 mmol) and triphenylphosphine (2 mmol) in benzene (30 ml) was added dropwise a solution of sodium hydride (5 mmol) in benzene (20 ml) under argon at room temperature and then the mixture was refluxed for 10 hours. The reaction mixture was poured into water and extracted with ethyl acetate. Organic layer was washed with dilute HCl, NaHCO_3

solution, water, and then dried over anhydrous MgSO_4 . After removal of the solvent, the residue was chromatographed with toluene-hexane (4:1) to give 2-ethoxycarbonylmethylene-3,3-diphenylindoline **19** (78 %), mp 109-110°; ir: ν (KBr) 3340, 1666, 1613, 1283, 1219; ^1H nmr: δ 1.23 (t, 3H, $J = 7.1$), 4.13 (q, 2H, $J = 7.1$), 4.89 (s, 1H), 6.84-6.91 (m, 2H), 7.11-7.30 (m, 12H), 10.0 (br s, 1H); ^{13}C nmr: δ 14.0, 58.8, 85.5, 109.0, 121.2, 125.1, 126.7, 128.1, 135.1, 142.6, 143.9, 168.0.

Anal. Calcd. for $\text{C}_{24}\text{H}_{21}\text{NO}_2$ (355.4): C, 81.10; H, 5.96; N, 3.94. Found: C, 80.82; H, 6.24; N, 3.66.

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