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ORIGINAL ARTICLE

Piperazine catalyzed convenient synthesis of 4*H*-pyran derivatives from α,α′-bis (substituted-benzylidene) cycloalkanones and malononitrile under reflux conditions

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Abstract A facile, simple and convenient method for the synthesis of 4*H*-pyran derivatives has been achieved through the condensation reactions of α,α′-bis(substituted-benzylidene) cycloalkanones and malononitrile in the presence of piperazine as an odorless and easy to work catalyst under reflux conditions. With the optimized reaction conditions, the desired products were obtained with 62–82% yields.

1. Introduction

Multifunctionalized 4*H*-pyrans have received considerable attention in previous years owing to wide range of useful biological and pharmacological properties such as anti-coagulant, anticancer, spasmolytic, and anti-anaphylactic activities (Foye, 1991; Green et al., 1995; Hatakeyama et al., 1988; Kang et al., 2009; Rong et al., 2006). These compounds can be employed as pigments (Ellis, 1977), photoactive materials (Armesto et al., 1989) and utilized as potential biodegradable agrochemicals (Abdelgalil et al., 1982; Hafez et al., 1987). Furthermore, 2-amino-4*H*-pyrans are useful for preparation of difficultly accessible annulated heterocycles (ÓCallaghan et al., 1995).

Several methods are available for the synthesis of 4*H*-pyrans especially 2-amino-4*H*-pyrans involving the bicomponent condensation of α-cyanocinnamonitriles with dimedone (Seifi and Sheiban, 2008) or β-naphthol (Wang et al., 2008), three-component reaction of aldehydes, malononitrile or ethyl cyanoacetate with dimedone (Wang et al., 2006), ethylacetoacetate (Valizadeh and Azimi, 2011), 4-hydroxycoumarin, 4-hydroxy-6-methylpyrone (Khurana et al., 2010) and active phenols (Gong et al., 2008). The other synthetic method for preparation of 2-amino-4*H*-pyran derivatives was achieved by the Michael

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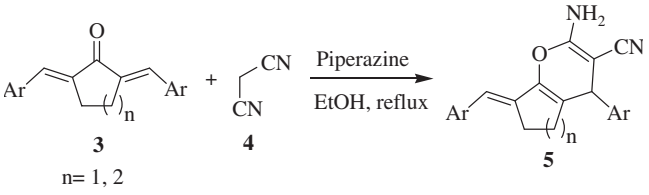


Scheme 1 Synthesis of 4*H*-pyran derivatives.

addition-cyclization reaction of α,β-unsaturated carbonyl compound with malononitrile (Zhao et al., 2009; Zhou, 2003; Kumar et al., 2007, 2011). However, some of these methods suffer from one or more disadvantages such as use of toxic organic solvents or toxic catalyst (such as piperidine (Zhou, 2003)), strong bases for example sodium ethoxide (Kumar et al., 2007), special reagents/apparatus, and often expensive catalysts. Although several methods for the synthesis of 4*H*-pyran derivatives have been reported, there is still a demand for simple and facile procedures for the preparation of these compounds using a cheap and readily available catalyst.

2. Results and discussion

As a part of our continued interest in the development of practical, safe and environmentally friendly procedures for some important transformations (Foroughifar et al., 2009, 2010, 2011; Mobinikhaledi et al., 2011), we report here a convenient and facile method for the synthesis of 4*H*-pyran derivatives **5** via a bicomponent reaction of α,α′-bis(substituted-benzylidene) cycloalkanones **3** and malononitrile **4** in the presence of piperazine under reflux conditions (Scheme 1).

α,α′-Bis(substituted-benzylidene) cycloalkanone derivatives **3** were prepared from Cross-Aldol condensation of cyclic ketones **1** with various aromatic aldehydes **2** bearing electron-withdrawing groups (such as nitro, halide), electron-releasing groups (such as methyl, methoxy), according to the reported procedures (Scheme 2) (Cai et al., 2006; Singh et al., 2009).

In order to optimize the reaction conditions, some polar and non polar solvents in the presence of piperazine have been used in reaction of 2,6-dibenzylidenecyclohexanone **3a** with malononitrile **4** as a model reaction to investigate the effects of solvent for preparing compound **5a** (Table 1). It is noteworthy to mention that the polar solvents such as methanol and ethanol or acetonitrile, afforded the better yields than nonpolar ones, and ethanol is the most effective solvent. In addition, increasing the loading of the catalyst to 20 mol% gave no improvement in the yield of **5a**, while reaction with 5 mol% of catalyst needed longer reaction time (Table 1, entry 8).

After determining the optimized reaction conditions, we turned our attention toward studying the scope of this reaction to test the generality of this method. Thus, various 2,6-dibenzylidenecyclohexanone derivatives with both activating and deactivating groups such as Me, OMe, F, Cl, and NO_2 were treated under the optimized conditions and afforded the corresponding 4*H*-pyran derivatives in good yields. To extend the preparative utility and generality of this reaction a variety of 2,5-dibenzylidenecyclopentanone derivatives were treated with malononitrile under the same experimental conditions and corresponding products were obtained in good yields without any difficulties (Table 2). The results clearly indicate that reactions can tolerate a wide range of differently substituted α,α′-bis(substituted-benzylidene) cycloalkanones **3**, and substituents on the aromatic ring did not show any electronic effects in terms of yields under these reaction conditions.

3. Conclusion

In conclusion, we have developed a low-cost, convenient procedure for the synthesis of 4*H*-pyran derivatives by a one-step condensation reaction of α,α′-bis(substituted benzylidene) cycloalkanones and malononitrile in the presence of piperazine under organic conditions.

4. Experimental

4.1. General experimental section

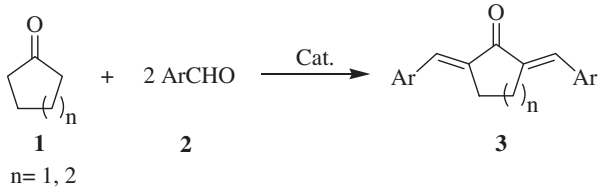
All products were characterized by a comparison of their spectral (IR, ^{1}H NMR, and ^{13}C NMR) data. Melting points were measured by using capillary tubes on an electro thermal digital apparatus and are uncorrected. IR spectra were recorded on a galaxy series FT-IR 5000 spectrometer in KBr pellet. ^{1}H NMR and ^{13}C NMR spectra were obtained from a solution in DMSO-d_6 with Me_4Si as internal standard using Brucker spectrophotometer (300 MHz).

4.2. General procedure for preparation of

A mixture of α,α′-bis(substituted benzylidene) cycloalkanones (1 mmol), malononitrile (1.5 mmol), piperazine (10 mol%) and 5 mL of ethanol was stirred magnetically under reflux conditions for appropriate time as mentioned in Table 2. After completion of the reaction as monitored by TLC, reaction mixture was cooled to room temperature and 10 mL of water was added to it. The solid product obtained was filtered and dried. The crude product was recrystallized from ethanol to yield pure product.

4.2.1. Spectral data

*4.2.1.1. Compound **5a** (Table 2, entry 1).* IR (KBr): ν_{max} = 3432, 3338, 3025, 2916, 2845, 2189, 1670, 1620, 1512, 1413, 1267, 1145, 1053, 700 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.41–7.19 (m, 10H, ArH), 6.97 (s, 1H, C=CH), 6.81 (s, 2H, NH_2), 3.97 (s, 1H, CH), 2.65–2.60 (m, 1H, CH_2), 2.50–2.46 (m, 1H, CH_2), 2.06–2.02 (m, 1H, CH_2) 1.85–1.80 (m, 1H, CH_2), 1.53–1.49 (m, 2H, CH_2); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 160.3, 144.4, 141.1, 137.2, 129.8, 129.5, 129.1, 128.8, 128.1, 127.4, 127.2, 122.6, 121.1, 116.0, 56.2 (C-CN), 43.6 (CH), 27.2 (CH_2), 26.9 (CH_2), 22.3 (CH_2); Anal. Calcd for $C_{23}H_{20}N_2O$: C, 81.15; H, 5.92; N, 8.23. Found: C, 80.97; H, 6.32; N, 8.17.



Scheme 2 α,α′-Bis(substituted-benzylidene) cycloalkanone derivatives.

Table 1 Optimization of reaction conditions.

Entry	Conditions	Piperazine (mol%)	Time (h)	Yield[a] (%)
1	Toluene/Reflux	10	6	53
2	CH_3OH/Reflux	10	3	76
3	CH_3CN/Reflux	10	3	73
4	$CHCl_3$/Reflux	10	4	65
5	CCl_4/Reflux	10	6	56
6	C_2H_5OH/R.T.	10	12	48
7	C_2H_5OH/Reflux	5	6	74
8	C_2H_5OH/Reflux	10	2.5	80
9	C_2H_5OH/Reflux	20	2.5	80

[a] Isolated yields.

Table 2 Synthesis of 4*H*-pyran derivatives.

Entry	Ar	*n*	Product	Time (h)	Yield[a] (%)	M.P (°C)
1	C_6H_5	2	**5a**	2.5	80	250–251
2	3,4-$(MeO)_2$ C_6H_3	2	**5b**	5	71	200–202
3	4-Me C_6H_4	2	**5c**	4	75	191–193
4	2-MeO C_6H_4	2	**5d**	6	62	181–183
5	4-Cl C_6H_4	2	**5e**	3.5	82	232–234
6	3-NO_2 C_6H_4	2	**5f**	5	81	265–266
7	2-Cl C_6H_4	2	**5g**	4	65	240–242
8	2-Cl-6-F C_6H_3	2	**5h**	6	73	237–238
9	C_6H_5	1	**5i**	3	78	235–236
10	3,4-$(MeO)_2$ C_6H_3	1	**5j**	6	65	186–187
11	2-Cl-6-F C_6H_3	1	**5k**	5	72	268–270
12	2-MeO C_6H_4	1	**5l**	5	66	185–187

[a] Isolated yields.

4.2.1.2. Compound ***5b*** *(Table 2, entry 2).* IR (KBr): ν_{max} = 3396, 3329, 2966, 2185, 1667, 1607, 1512, 1462, 1417, 1248, 1134, 1024, 891, 781 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ = 6.97–6.86 (m, 5H, ArH), 6.77–6.71 (m, 2H, ArH, C=CH), 6.68 (s, 2H, NH_2), 3.91 (s, 1H, CH), 3.76 (s, 6H, OCH_3), 3.74 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 2.71–2.65 (m, 1H, CH_2), 2.54–2.50 (m, 1H, CH_2), 2.06–2.00 (m, 1H, CH_2) 1.85–1.79 (m, 1H, CH_2), 1.56–1.49 (m, 2H, CH_2); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 160.2, 149.2, 148.8, 148.3, 141.1, 137.0, 130.0, 128.3, 122.4, 122.2, 121.2, 120.1, 115.3, 113.3, 112.5, 122.1, 111.9, 56.6 (C-CN), 56.0 (OCH_3), 55.9 (OCH_3), 55.8 (OCH_3), 43.2 (CH), 27.2 (CH_2), 27.1 (CH_2), 22.4 (CH_2). Anal. Calcd for $C_{27}H_{28}N_2O_5$: C, 70.42; H, 6.13; N, 6.08. Found: C, 70. 28; H, 6.21; N, 6.03.

4.2.1.3. Compound ***5c*** *(Table 2, entry 3).* IR (KBr): ν_{max} = 3445, 3333, 3040, 2918, 2195, 1667, 1638, 1601, 1508, 1406, 1253, 1126, 1040, 879 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ = 7.20–7.08 (m, 8H, ArH), 6.93 (s, 1H, C=CH), 6.78 (s, 2H, NH_2), 3.90 (s, 1H, CH), 2.61–2.58 (m, 1H, CH_2), 2.49–2.45 (m, 1H, CH_2), 2.28 (s, 6H, CH_3), 2.04–1.97 (m, 1H, CH_2) 1.80–1.75 (m, 1H, CH_2), 1.48 (s, 2H, CH_2); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 160.2, 141.5, 141.0, 136.5, 134.4, 129.6, 129.5, 129.4, 129.1, 128.0, 122.4, 121.1, 115.7, 56.5 (C-CN), 43.3 (CH), 27.2 (CH_2), 27.0 (CH_2), 22.3 (CH_2), 21.2 (CH_3), 21.1 (CH_3); Anal. Calcd for $C_{25}H_{24}N_2O$: C, 81.49; H, 6.57; N, 7.60. Found: C, 81.31; H, 6.53; N, 7.65.

4.2.1.4. Compound ***5d*** *(Table 2, entry 4).* IR (KBr): ν_{max} = 3458, 3347, 2935, 2835, 2189, 1672, 1634, 1597, 1489, 1462, 1246, 1128, 1026, 754 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ = 7.25–7.19 (m, 3H, ArH), 7.08 (s, 1H, C=CH), 7.02–6.93 (m, 5H, ArH), 6.67 (s, 2H, NH_2), 4.45 (s, 1H, CH), 3.80 (s, 6H, OCH_3), 2.42–2.37 (m, 1H, CH_2), 2.08–1.94 (m, 2H, CH_2), 1.80–1.75 (m, 1H, CH_2) 1.51–1.44 (m, 2H, CH_2); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 160.9, 157.4, 157.3, 141.5, 132.4, 130.4, 129.6, 129.0, 128.9, 128.5, 125.8, 121.5, 121.2, 120.3, 118.5, 115.7, 111.8, 111.2, 56.2 (C-CN), 55.8 (OCH_3), 55.6 (OCH_3), 35.6 (CH), 27.2 (CH_2), 27.1(CH_2), 22.4 (CH_2); Anal. Calcd for $C_{25}H_{24}N_2O_3$: C, 74.98; H, 6.04; N, 7.00. Found: C, 75.11; H, 6.10; N, 6.93.

4.2.1.5. Compound ***5e*** *(Table 2, entry 5).* IR (KBr): ν_{max} = 3454, 3315, 2187, 1672, 1632, 1597, 1487, 1410, 1263, 1134, 1013, 895, 823 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ = 7.45–7.40 (m, 4H, ArH), 7.32 (d, J = 8.3 Hz, 2H, ArH), 7.23 (d, J = 8.2 Hz, 2H, ArH), 6.94 (s, 1H, C=CH), 6.82 (s, 2H, NH_2), 4.02 (s, 1H, CH), 2.64–2.59 (m, 1H, CH_2), 2.50–2.46 (m, 1H, CH_2), 2.05–2.00 (m, 1H, CH_2) 1.79–1.74 (m, 1H, CH_2), 1.53 (s, 2H, CH_2); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 160.3, 143.4, 141.0, 136.0, 132.0, 131.9, 131.2, 130.5, 129.9, 129.1, 128.8, 121.4, 120.9, 116.0, 55.8 (C-CN), 42.9 (CH), 27.1 (CH_2), 26.8 (CH_2), 22.2 (CH_2); Anal. Calcd for $C_{23}H_{18}Cl_2N_2O$: C, 67.49; H, 4.43; N, 6.84. Found: C, 67.34; H, 4.52; N, 6.95.

4.2.1.6. Compound ***5f*** *(Table 2, entry 6)*. Yield 81%; time 5 h; mp = 265–266 °C; IR (KBr): ν_{max} = 3439, 3331, 3219, 2930, 2193, 1676, 1645, 1605, 1520, 1419, 1350, 1136, 1041, 812, 731 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ = 8.16–8.06 (m, 4H, ArH), 7.77–7.68 (m, 4H, ArH), 7.09 (s, 1H, C=CH), 6.97 (s, 2H, NH_2), 4.31 (s, 1H, CH), 2.73–2.68 (m, 1H, CH_2), 2.55–2.50 (m, 1H, CH_2), 2.10–2.05 (m, 1H, CH_2) 1.81–1.75 (m, 1H, CH_2), 1.57 (s, 2H, CH_2); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 160.5, 148.5, 148.3, 146.6, 141.2, 138.7, 135.7, 134.9, 132.1, 130.9, 130.3, 123.8, 122.7, 122.5, 121.9, 120.9, 120.6, 116.5, 55.4 (C-CN), 43.1 (CH), 27.0 (CH_2), 26.7 (CH_2), 22.1 (CH_2); Anal. Calcd for $C_{23}H_{18}N_4O_5$: C, 64.18; H, 4.22; N, 13.02. Found: C, 64.31; H, 4.31; N, 12.94.

4.2.1.7. Compound ***5g*** *(Table 2, entry 7)*. IR (KBr): ν_{max} = 3464, 3345, 3055, 2920, 2191, 1670, 1637, 1595, 1468, 1414, 1255, 1130, 1034, 748 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ = 7.50–7.27 (m, 8H, ArH), 6.99 (s, 1H, C=CH), 6.94 (s, 2H, NH_2), 4.58 (s, 1H, CH), 2.45–2.34 (m, 2H, CH_2), 2.09–2.02 (m, 1H, CH_2), 1.74–1.68 (m, 1H, CH_2), 1.50–1.45 (m, 2H, CH_2); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 160.6, 141.3, 141.2, 135.3, 133.4, 132.9, 131.5, 131.4, 130.9, 129.9, 129.8, 129.2, 128.5, 127.3, 120.7, 119.9, 115.8, 55.1 (C-CN), 40.1 (CH), 27.1 (CH_2), 27.0 (CH_2), 22.2 (CH_2); Anal. Calcd for $C_{23}H_{18}Cl_2N_2O$: C, 67.49; H, 4.43; N, 6.84. Found: C, 67.41; H, 4.50; N, 6.78.

4.2.1.8. Compound ***5h*** *(Table 2, entry 8)*. IR (KBr): ν_{max} = 3455, 3344, 2941, 2189, 1674, 1640, 1599, 1442, 1242, 1132, 901, 783 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ = 7.38–7.23 (m, 6H, ArH), 6.90 (s, 2H, NH_2), 6.64 (s, 1H, C=CH), 4.80 (s, 1H, CH), 2.15–2.02 (m, 3H, CH_2), 1.80–1.72 (m, 1H, CH_2), 1.51 (s, 2H, CH_2); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 161.4, 161.1, 158.1, 141.2, 134.4, 134.3, 134.1, 130.4, 130.3, 125.8, 124.2, 123.9, 120.6, 115.9, 115.2, 114.9, 113.1, 52.6 (C-CN), 40.2 (CH), 27.5 (CH_2), 27.0 (CH_2), 21.9 (CH_2); Anal. Calcd for $C_{23}H_{16}Cl_2F_2N_2O$: C, 62.04; H, 3.62; N, 6.29. Found: C, 61.90; H, 3.67; N, 6.19.

4.2.1.9. Compound ***5i*** *(Table 2, entry 9)*. IR (KBr): ν_{max} = 3447, 3331, 3248, 3204, 3020, 2918, 2845, 2197, 1684, 1643, 1587, 1450, 1383, 1109, 1043, 869, 756, 700 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ = 7.37–7.7.33 (m, 5H, ArH), 7.28–7.19 (m, 5H, ArH), 6.94 (s, 2H, NH_2), 6.38 (s, 1H, C=CH), 4.28 (s, 1H, CH), 2.80 (s, 2H, CH_2), 2.36–2.30 (m, 1H, CH_2), 2.10–1.98 (m, 1H, CH_2); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 161.2, 146.0, 143.1, 138.0, 137.4, 129.4, 129.1, 128.4, 128.1, 127.6, 126.9, 122.8, 121.1, 116.6, 56.3 (C-CN), 41.1 (CH), 28.1 (CH_2), 26.9 (CH_2); Anal. Calcd for $C_{22}H_{18}N_2O$: C, 80.96; H, 5.56; N, 8.58. Found: C, 81.05; H, 5.64; N, 8.51.

4.2.1.10. Compound ***5j*** *(Table 2, entry 10)*. IR (KBr): ν_{max} = 3400, 3329, 3211, 2939, 2179, 1684, 1637, 1593, 1512, 1462, 1421, 1250, 1134, 1026, 887, 771 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ = 6.95–6.85 (m, 6H, ArH), 6.75 (s, 2H, NH_2), 6.32 (s, 1H, C=CH), 4.20 (s, 1H, CH), 3.73 (s, 12H, OCH_3), 2.86–2.78 (m, 2H, CH_2), 2.35–2.30 (m, 1H, CH_2), 2.12–2.06 (m, 1H, CH_2); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 161.1, 149.2, 149.1, 148.3, 148.1, 146.0, 135.7, 130.5, 121.7, 121.1, 120.1, 116.5, 112.4, 111.9, 111.8, 56.8 (C-CN), 56.0 (OCH_3), 55.8 (OCH_3), 28.1 (CH_2), 26.7 (CH_2); Anal. Calcd for $C_{26}H_{26}N_2O_5$: C, 69.94; H, 5.87; N, 6.27. Found: C, 69.85; H, 5.95; N, 6.18.

4.2.1.11. Compound ***5k*** *(Table 2, entry 11)*. IR (KBr): ν_{max} = 3481, 3331, 3210, 2911, 2197, 1689, 1643, 1597, 1445, 1377, 1242, 1107, 1038, 895, 781 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ = 7.41–7.21 (m, 6H, ArH), 7.04 (s, 2H, NH_2), 6.26 (s, 1H, C=CH), 4.98 (s, 1H, CH), 2.45 (s, 2H, CH_2), 2.36–2.29 (m, 1H, CH_2), 2.02–1.96 (m, 1H, CH_2) ^{13}C NMR (75 MHz, DMSO-d_6): δ = 161.4, 158.1, 146.2, 142.8, 134.2, 134.1, 130.6, 130.5, 130.0, 129.9, 125.8, 123.9, 123.7, 122.3, 120.5, 115.4, 115.1, 107.1, 53.4 (C-CN), 35.4 (CH), 27.3 (CH_2), 26.2 (CH_2); Anal. Calcd for $C_{22}H_{14}Cl_2F_2N_2O$: C, 61.27; H, 3.27; 8.81; N, 6.50. Found: C, 61.15; H, 3.36; N, 6.46.

4.2.1.12. Compound ***5l*** *(Table 2, entry 12)*. IR (KBr): ν_{max} = 3331, 3211, 3061, 2914, 2193, 1682, 1640, 1593, 1487, 1464, 1365, 1236, 1101, 1030, 748 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ = 7.39–7.09 (m, 5H, ArH), 6.99–6.92 (m, 5H, ArH, NH_2), 6.68 (s, 1H, C=CH), 4.69 (s, 1H, CH), 3.72 (s, 6H, OCH_3), 2.72 (s, 2H, CH_2), 2.35–2.30 (m, 1H, CH_2), 2.03–1.98 (m, 1H, CH_2); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 161.9, 157.2, 156.8, 146.5, 137.4, 130.8, 128.9, 128.6, 128.3, 128.0, 126.1, 122.4, 121.4, 121.2, 120.7, 111.6, 111.3, 110.6, 56.0 (C-CN), 55.8 (OCH_3), 55.4 (OCH_3), 33.9 (CH), 28.1 (CH_2), 26.7 (CH_2); Anal. Calcd for $C_{24}H_{22}N_2O_3$: C, 74.59; H, 5.74; N, 7.25. Found: C, 74.69; H, 5.81; N, 7.14.

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