An Efficient One-pot Synthesis of Polyhydrobenzoacridine-1-one Derivatives under Microwave Irradiation without Catalyst

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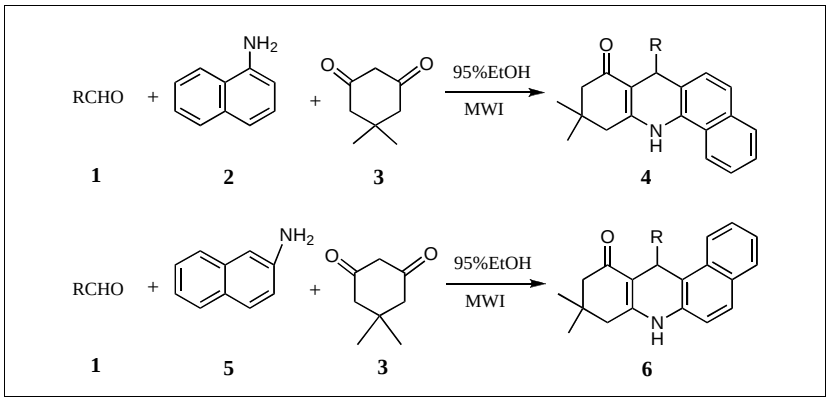

A series of 3,3-dimethyl-9-substituted-1,2,3,4,9,10-hexahydrobenzo[*c*]acridine-1-ones and 3,3-dimethyl-9-substituted-1,2,3,4,9,10-hexahydrobenzo[*a*]acridine-1-ones were synthesized by the reaction of an aldehyde, α−naphthylamine or β−naphthylamine and dimedone under microwave irradiation with short times and high yields.

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A lot of natural and synthetic compounds containing the acridine skeleton display interesting biological and physical activities, such as antimalaria [1] and antitumor agents [2], and multihydroacridineone derivatives have been reported to have high fluorescence efficiency and can be used as fluorescent molecular probes for monitoring of polymerization process [3]. They are also increasingly receiving attention due to their likeness in properties with those of 1,4-dihydropyridines, which have similarities in structure to the biologically important compounds such as NADH and NADPH [4]. As a consequence, the interest of organic chemists in the synthesis or structure modifications of acridinedione derivatives remains high. Recently, there are many other methods available for the construction of benzoacridine derivatives, for instance, by refluxing appropriate naphthylamine, dimedone and aldehyde in C_6H_6 [5], EtOH [6,7] or H_2O [8,9]. But these reactions need long reaction times (2-18 hours) [5,8] and complicated route that naphthylamine and aldehyde need to be condensed to schiff's base firstly [8]. Microwave irradiation (MWI) is a very useful technique in organic synthesis [10]. It is a simple, timesaving, high yielding, and environmentally friendly process. We have already reported the synthesis of heterocyclic compounds under microwave irradiation [11]. M. Kidwai and S. Rastogi have reported the synthesis of polyhydroacridinones without additional fused benzene rings [12]. Here, we would like to report a highly efficient method for the one-pot synthesis of a series of 3,3-dimethyl-9-substituted-1,2,3,4,9,10-hexahydrobenzo[*c*]acridine-1-ones and 3,3-dimethyl-9-substituted-1,2,3,4,9,10-hexahydrobenzo[*a*]acridine-1-ones under microwave irradiation without catalyst.

The products were synthesized by equimolecular amounts of naphthylamine, dimedone and aldehyde without catalyst in a small amount of ethanol (95%) under microwave irradiation (Scheme 1). After irradiation for 4-19 min, the polyhydrobenzoacridine-1-one derivatives were obtained in excellent yields (75-98%). Besides, compared with the traditional heating methodology, when **1a**, **2** and **3** in ethanol were irradiated with microwave, the reaction time was shortened to 6 min from 12 hours [8,9]. The results were listed in Table 1 and Table 2.

Results and Discussion.

The procedure is easy to operate and the workup procedure is just simple filtrations. Furthermore, we found that this protocol can be applied not only for the aromatic aldehydes with either electron-withdrawing groups or electron-donating groups, but also for heterocyclic and aliphatic aldehydes.

Table 1

Physical Data of Compounds **4**

Compound No.	R	Microwave-assisted			Conventional[d]	
		Time (lit.) (min)	Yield (lit.) (%)[a]	Mp (lit.) (℃)[b]	Reaction time (h)	Yield (%)
4a	4-ClC_6H_4	6 (12h)[c]	98(93)[c]	276-277 (263-266)[c]	2	85
4b	4-BrC_6H_4	7 (12h)[c]	92 (91)[c]	276.6-277 (276-278)[c]	2.5	81
4c	2-ClC_6H_4	6 (12h)[c]	98 (98)[c]	>300 (273-275)[c]	2	88
4d	4-FC_6H_4	13	82	269.2-271	3	75
4e	2,4-$Cl_2C_6H_3$	11(12h)[c]	87	>300 (280-282)[c]	3	78
4f	3,4-$Cl_2C_6H_3$	16 (12h)[c]	92 (90)[c]	>300 (284-286)[c]	3	73
4g	3, 4-$OCH_2OC_6H_3$	19 (18h)[c]	95 (89)[c]	>300 (283-285)[c]	3.5	85
4h	4-$OCH_3C_6H_4$	13 (18h)[c]	93 (89)[c]	257-259 (260-262)[c]	3	81
4i	2, 3-$(CH_3O)_2C_6H_3$	9	95	298-299	2	88
4j	3, 4-$(CH_3O)_2C_6H_3$	14 (18h)[c]	93 (93)[c]	255-256 (246-247)[c]	2.5	80
4k	3-CH_3O-4-OHC_6H_4	16	85	270-273	2.5	78
4l	4-$NO_2C_6H_4$	7	95 (93)[c]	295-296 (280-282)[c]	2	82
4m	3-$NO_2C_6H_4$	11 (12h)[c]	95 (95)[c]	280-283 (267-269)[c]	2.5	86
4n	C_4H_3S	6	75	259-261	2	71
4o	$CH_3(CH_2)_3$	15	80	162-164	3	72

.

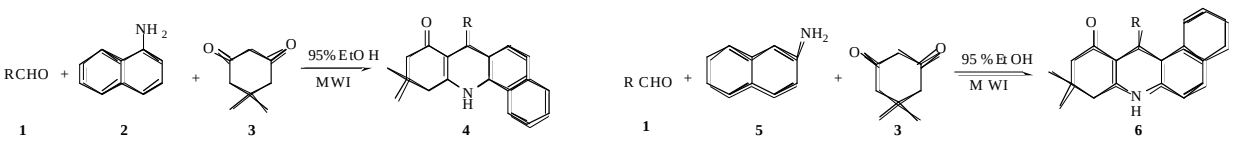
Table 2

Physical Data of Compounds **6**

Compound No.	R	Microwave-assisted			Conventional[d]	
		Time (min) (lit.)	Yield (lit.) (%)[a]	Mp (lit.) (℃)[b]	Reaction time (h)	Yield (%)
6a	4-ClC_6H_4	8 (3h)[c]	98 (98)[c]	>300 (>300)[c]	1.5	85
6b	4-BrC_6H_4	8 (4h)[c]	95 (87)[c]	>300	1.5	81
6c	4-$OCH_3C_6H_4$	9 (5h)[c]	98 (97)[c]	>300 (297-298)[c]	2	85
6d	3, 4-$OCH_2OC_6H_3$	4	93	>300	1	79
6e	3, 4-$(CH_3O)_2C_6H_3$	5 (10h)[c]	97(96)[c]	293-296	1.5	86
6f	C_6H_5	6	93	>300	1.5	79
6g	4-$NO_2C_6H_4$	8	92	246-248	2	78
6h	3-$NO_2C_6H_4$	9	92	294-296	2	78
6i	3-CH_3O-4-OHC_6H_4	4 (12h)[c]	92 (99)[c]	296-298	1	77
6j	C_4H_3S	5 (5h)[c]	98 (98)[c]	>300	1	85
6k	4-(benzo[*d*]oxazol-2-yl)C_6H_4	5	96	>300	1	84
6l	3-indole	7	90	>300	2	79
6m	$CH_3(CH_2)_3$	9	81	186-188	2	72

[a] Yields of isolated compounds; [b] Melting points are uncorrected; [c] Known compounds (**4a**, **4b**, **4c**, **4h**, **4l**, **6a**, **6c**, **6e**, **6i**, **6j**, ref. 8; **4b**, **4c**, **4h**, **4l**, **6a**, ref. 5; **4e**, **4f**, **4g**, **4j**, **4m**, ref. 9; **6c**, ref. 7; [d] The time and the yield of the reaction by the traditonal thermal mode at 80°C.

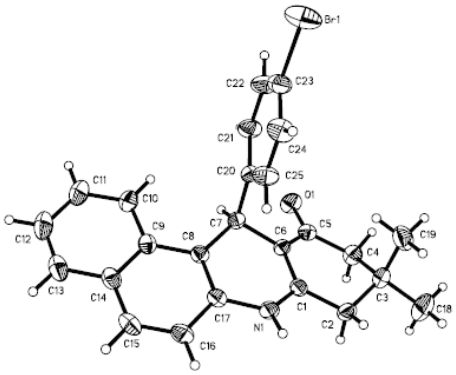
Scheme 1



From Table 1 and Table 2, we find that microwave-assisted reaction exhibited several advantages over conventional heating by not only significantly reducing the reaction time but also by improving the reaction yield dramatically.

All the products were characterized by IR, ^{1}H NMR and elemental analysis. Furthermore, the structure of **6b** was established by an X-ray crystallographic analysis [13] (Figure 1).

Figure 1



In conclusion, we have disclosed a facile case, using microwave heating mode in a small amount of ethanol without catalyst. The one-pot synthesis of hexahydrobenzoacridine-1-one derivatives has the notable advantages of wide applicability, short route and reaction time, high yield, easy workup procedure and being environmentally friendly.

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EXPERIMENTAL

Microwave irradiation was carried out in a modified commercial microwave oven (2450 MHz, Nanjing Sanle) under atmospheric pressure in a ventilating arrangement. Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on a TENSOR 27 spectrometer in KBr. ^{1}H NMR spectra were measured on a DPX 400 spectrometer operating at 400 MHz, using DMSO-d_6 as solvent and TMS as internal standard. Elemental analyses were determined by using a Perkin-Elmer 240c elemental analysis instrument.

General Procedure for 3,3-Dimethyl-9-substituted-1,2,3,4,9,10-hexahydrobenzo[*c*]acridine-1-ones (**4**).

A solution of the appropriate aldehyde (2 mmol), dimedone (2 mmol), α-naphthylamine (2 mmol) and in ethanol (3 mL) was irradiated for 6-19 min with power 220 W. The reaction mixture was cooled to room temperature, then poured into water (50 mL), filtered to give the crude product, which was further purified by recrystallization from EtOH (**4a**-**4o**). All the products were characterized by IR, ^{1}H NMR and elemental analysis.

3,3-Dimethyl-9-(4-chlorophenyl)-1,2,3,4,9,10-hexahydrobenzo-[*c*]acridine-1-one, (**4a**).

This compound was obtained according to above general procedure; ir (potassium bromide): 3334, 2958, 1605, 1572, 1492, 1374, 1262, 1148, 1090, 1014, 851, 822, 757 cm^{-1}; ^{1}H nmr (DMSO-d_6): δ 9.30 (s, 1H, NH), 8.46 (d, 1H, J = 8.8 Hz, ArH), 7.82 (d, 1H, J = 7.6 Hz, ArH), 7.58–7.56 (m, 1H, ArH), 7.52–7.46 (m, 2H, ArH), 7.26-7.23 (m, 5H, ArH), 5.22 (s, 1H, CH), 2.73 (d, 1H, J = 16.0 Hz, CH), 2.66 (d, 1H, J = 16.8 Hz, CH), 2.25 (d, 1H, J = 16.0 Hz, CH), 2.05 (d, 1H, J = 16.0 Hz, CH), 1.08 (s, 3H, CH_3), 0.98 (s, 3H, CH_3).

Anal. Calcd. for $C_{25}H_{22}ClNO$: C, 77.41; H, 5.72; N, 3.61. Found: C, 77.52; H, 5.66; N, 3.71.

3,3-Dimethyl-9-(4-bromophenyl)-1,2,3,4,9,10-hexahydrobenzo-[c]acridine-1-one, (**4b**).

This compound was obtained according to above general procedure; ir (potassium bromide): 3306, 2947, 1588, 1518, 1382, 1260, 1151, 1066, 1010, 850, 806, 755 cm^{-1}; ^{1}H nmr (DMSO-d_6): δ 9.30 (s, 1H, NH), 8.48 (d, 1H, J = 8.2 Hz, ArH), 7.83 (d, 1H, J = 7.6 Hz, ArH), 7.60–7.36 (m, 5H, ArH), 7.26-7.16 (m, 3H, ArH), 5.22(s, 1H, CH), 2.74 (d, 1H, J = 17.2 Hz, CH), 2.66 (d, 1H, J = 16.8 Hz, CH), 2.25 (d, 1H, J = 16.0 Hz, CH), 2.05 (d, 1H, J = 16.0 Hz, CH), 1.10 (s, 3H, CH_3), 1.01 (s, 3H, CH_3).

Anal. Calcd. for $C_{25}H_{22}BrNO$: C, 69.45; H, 5.13; N, 3.24. Found: C, 69.56; H, 5.09; N, 3.44.

3,3-Dimethyl-9-(2-chlorophenyl)-1,2,3,4,9,10-hexahydrobenzo-[*c*]acridine-1-one, (**4c**).

This compound was obtained according to above general procedure; ir (potassium bromide): 3303, 2960, 1588, 1517,1390, 1264, 1148, 1061, 1034, 802, 745, 730 cm^{-1}; ^{1}H nmr (DMSO-d_6): δ 9.27 (s, 1H, NH), 8.47 (d, 1H, J = 8.8 Hz, ArH), 7.80 (d, 1H, J = 8.0 Hz, ArH), 7.58–7.43 (m, 3H, ArH), 7.36–7.26 (m, 3H, ArH), 7.16-7.09 (m, 2H, ArH), 5.74 (s, 1H, CH), 2.77 (d, 1H, J = 16.0 Hz, CH), 2.69 (d, 1H, J = 16.0 Hz, CH), 2.24 (d, 1H, J = 16.0 Hz, CH), 2.02 (d, 1H, J = 16.0 Hz, CH), 1.10 (s, 3H, CH_3), 1.04 (s, 3H, CH_3).

Anal. Calcd. for $C_{25}H_{22}ClNO$: C, 77.41; H, 5.72; N, 3.61. Found: C, 77.66; H, 5.52; N, 3.65.

3,3-Dimethyl-9-(4-fluorophenyl)-1,2,3,4,9,10-hexahydrobenzo-[*c*]acridine-1-one, (**4d**)

This compound was obtained according to above general procedure; ir (potassium bromide): 3318, 2957, 1678, 1589, 1518,1384, 1263, 1152, 1092, 1061, 842, 813, 752 cm^{-1}; ^{1}H nmr (DMSO-d_6): δ 9.29 (s, 1H, NH), 8.48 (d, 1H, J = 8.4 Hz, ArH), 7.83 (d, 1H, J = 8.0 Hz, ArH), 7.58–7.56 (m, 1H, ArH), 7.48-7.46 (m, 2H, ArH), 7.28-7.21 (m, 2H, ArH), 7.00-6.97 (m, 3H, ArH), 5.24 (s, 1H, CH), 2.74 (d, 1H, J = 16.0 Hz, CH), 2.66 (d, 1H, J = 16.0 Hz, CH), 2.24 (d, 1H, J = 16.0 Hz, CH), 2.05 (d, 1H, J = 16.0 Hz, CH), 1.07 (s, 3H, CH_3), 0.96 (s, 3H, CH_3).

Anal. Calcd. for $C_{25}H_{22}FNO$: C, 80.84; H, 5.97; N, 3.77. Found: C, 80.93; H, 5.88; N, 3.51.

3,3-Dimethyl-9-(2,4-dichlorophenyl)-1,2,3,4,9,10-hexahydrobenzo[*c*]acridine-1-one, (**4e**).

This compound was obtained according to above general procedure; ir (potassium bromide): 3304, 2960, 1684, 1590, 1518,1385, 1262, 1149, 1095, 1037, 880, 807, 754 cm^{-1}; ^1H nmr (DMSO-d_6): δ 9.34 (s, 1H, NH), 8.47 (d, 1H, J = 8.4 Hz, ArH), 7.82 (d, 1H, J = 8.0 Hz, ArH), 7.62–7.40 (m, 4H, ArH), 7.25-7.18 (m, 3H, ArH), 5.71(s, 1H, CH), 2.78 (d, 1H, J = 16.0 Hz, CH), 2.70 (d, 1H, J = 16.0 Hz, CH), 2.25 (d, 1H, J = 16.0 Hz, CH), 2.04 (d, 1H, J = 16.0 Hz, CH), 1.10 (s, 3H, CH_3), 1.05 (s, 3H, CH_3).

Anal. Calcd. for $C_{25}H_{21}Cl_2NO$: C, 71.10; H, 5.01; N, 3.32. Found: C, 71.31; H, 5.11; N, 3.29.

3,3-Dimethyl-9-(3,4-dichlorophenyl)-1,2,3,4,9,10-hexahydrobenzo[*c*]acridine-1-one, (**4f**).

This compound was obtained according to above general procedure; ir (potassium bromide): 3311, 2953, 1592, 1518,1390, 1262, 1151, 1060, 1029, 884, 811, 761, 633 cm^{-1}; ^1H nmr (DMSO-d_6): δ 9.36 (s, 1H, NH), 8.48 (d, 1H, J = 8.4 Hz, ArH), 7.84 (d, 1H, J = 8.0 Hz, ArH), 7.59 (t, 1H, J = 8.0 Hz, ArH), 7.54 -7.44 (m, 4H, ArH), 7.30 (d, 1H, J = 8.0 Hz, ArH), 7.18-7.15 (m, 1H, ArH), 5.28 (s, 1H, CH), 2.76 (d, 1H, J = 16.0 Hz, CH), 2.71 (d, 1H, J = 16.0 Hz, CH), 2.26 (d, 1H, J = 16.0 Hz, CH), 2.06 (d, 1H, J = 16.0 Hz, CH), 1.08 (s, 3H, CH_3), 0.99 (s, 3H, CH_3).

Anal. Calcd. for $C_{25}H_{21}Cl_2NO$: C, 71.10; H, 5.01; N, 3.32. Found: C, 71.25; H, 5.09; N, 3.18.

3,3-Dimethyl-9-(3,4-methylenedioxylphenyl)-1,2,3,4,9,10-hexa–hydrobenzo[*c*]acridine-1-one, (**4g**).

This compound was obtained according to above general procedure; ir (potassium bromide): 3329, 2956, 1585, 1518,1392, 1230, 1151, 1038, 1030, 883, 814, 765, 640 cm^{-1}; ^1H nmr (DMSO-d_6): δ 9.25 (s, 1H, NH), 8.46 (d, 1H, J = 8.4 Hz, ArH), 7.83 (d, 1H, J = 8.0 Hz, ArH), 7.59-7.46 (m, 3H, ArH), 7.29 (d, 1H, J = 8.8 Hz, ArH), 6. 76-6. 64 (m, 3H, ArH), 5.88 (d, 2H, J = 10.8 Hz, CH), 5.13(s, 1H, CH), 2.74 (d, 1H, J = 17.2 Hz, CH), 2.65 (d, 1H, J = 17.2 Hz, CH),2.24 (d, 1H, J = 16.0 Hz, CH), 2.06 (d, 1H, J = 16.0 Hz, CH), 1.08 (s, 3H, CH_3), 1.01 (s, 3H, CH_3).

Anal. Calcd. for $C_{26}H_{23}NO_3$: C, 78.57; H, 5.83; N, 3.52. Found: C, 78.34; H, 5.98; N, 3.48.

3,3-Dimethyl-9-(4-methoxyphenyl)-1,2,3,4,9,10-hexahydrobenzo[*c*]acridine-1-one, (**4h**).

This compound was obtained according to above general procedure; ir (potassium bromide): 3350, 2954, 1591, 1496, 1384, 1254, 1149, 1384, 1254, 1149, 1036, 831, 807, 765, 646 cm^{-1}; ^1H nmr (DMSO-d_6): δ 9.23 (s, 1H, NH), 8.46 (d, 1H, J = 8.8 Hz, ArH), 7.82 (d, 1H, J = 8.0 Hz, ArH), 7.59-7.44 (m, 3H, ArH), 7.25 (d, 1H, J = 8.4 Hz, ArH), 7.12 (d, 2H, J = 8.4 Hz, ArH), 6.73 (d, 2H, J = 8.4 Hz, ArH), 5.14 (s, 1H, CH), 3.64 (s, 3H, OCH_3), 2.73 (d, 1H, J = 16.8 Hz, CH), 2.65 (d, 1H, J = 16.8 Hz, CH), 2.24 (d, 1H, J = 16.0 Hz, CH), 2.04 (d, 1H, J = 16.0 Hz, CH), 1.08 (s, 3H, CH_3),1.00 (s, 3H, CH_3).

Anal. Calcd. for $C_{26}H_{25}NO_2$: C, 81.43; H, 6.57; N, 3.65. Found: C, 81.55; H, 6.34; N, 3.59.

3,3-Dimethyl-9-(2,3-dimethoxyphenyl)-1,2,3,4,9,10-hexahydro–benzo[*c*]acridine-1-one, (**4i**).

This compound was obtained according to above general procedure; ir (potassium bromide): 3314, 2951, 1588, 1517,1392, 1266, 1151, 1062, 826, 808, 762, 618 cm^{-1}; ^1H nmr (DMSO-d_6): δ 9.17 (s, 1H, NH), 8.43 (d, 1H, J = 8.8 Hz, ArH), 7.78 (d, 1H, J = 8.0 Hz, ArH), 7.55 (t, 1H, J = 8.0 Hz, ArH), 7.46 (d, 1H, J = 8.0 Hz, ArH), 7.40 (d, 1H, J = 8.4 Hz, ArH), 7.29 (d, 1H, J = 8.4 Hz, ArH), 6.84 (t, 1H, J = 8.0 Hz, ArH), 6.74-6.69 (m, 2H, ArH), 5.63 (s, 1H, CH), 3.97 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 2.78(d, 1H, J = 16.0 Hz, CH), 2.68 (d, 1H, J = 16.0 Hz, CH), 2.25 (d, 1H, J = 16.0 Hz, CH), 2.04 (d, 1H, J = 16.0 Hz, CH), 1.11 (s, 3H, CH_3), 1.08 (s, 3H, CH_3).

Anal. Calcd. for $C_{27}H_{27}NO_3$: C, 78.42; H, 6.58; N, 3.39. Found: C, 78.62; H, 6.34; N, 3.51.

3,3-Dimethyl-9-(3,4-dimethoxyphenyl)-1,2,3,4,9,10-hexahydrobenzo[*c*]acridine-1-one, (**4j**).

This compound was obtained according to above general procedure; ir (potassium bromide): 3350, 2930, 1591, 1518,1384, 1264, 1034, 767 cm^{-1}; ^1H nmr (DMSO-d_6): δ 9.25 (s, 1H, NH), 8.45 (d, 1H, J = 8.4 Hz, ArH), 7.82 (d, 1H, J = 8.0 Hz, ArH), 7.59-7.45 (m, 3H, ArH), 7.33 (d, 1H, J = 8.4 Hz, ArH), 6.90 (s, 1H, ArH), 6.74-6.54 (m, 2H, ArH), 5.14 (s, 1H, CH), 3.66 (s, 3H, OCH_3), 3.63 (s, 3H, OCH_3), 2.74 (d, 1H, J = 16.8 Hz, CH), 2.66 (d, 1H, J = 17.2 Hz, CH), 2.26 (d, 1H, J = 16.0 Hz, CH), 2.06 (d, 1H, J = 16.0 Hz, CH), 1.10 (s, 3H, CH_3), 1.04 (s, 3H, CH_3).

Anal. Calcd. for $C_{27}H_{27}NO_3$: C, 78.42; H, 6.58; N, 3.39. Found: C, 78.55; H, 6.37; N, 3.48.

3,3-Dimethyl-9-(4-hydroxy-3-methoxyphenyl)-1,2,3,4,9,10-hexa-hydrobenzo[*c*]acridine-1-one, (**4k**).

This compound was obtained according to above general procedure; ir (potassium bromide): 3289, 2960, 1567, 1496, 1394, 1262, 1062, 1092, 873, 810, 773, 644 cm^{-1}; ^1H nmr (DMSO-d_6): δ 9.25 (s, 1H, NH), 8.64 (s, 1H, OH), 8.44 (d, 1H, J = 8.8 Hz, ArH), 7.82 (d, 1H, J = 8.4 Hz, ArH), 7.57-7.45 (m, 3H, ArH), 7.32 (d, 1H, J = 8.4 Hz, ArH), 6.85 (s, 1H, ArH), 6.55 (s, 2H, ArH), 5.09 (s, 1H, CH), 3.67 (s, 3H, OCH_3), 2.73(d, 1H, J = 16.0 Hz, CH), 2.65 (d, 1H, J = 16.0 Hz, CH), 2.25 (d, 1H, J = 16.0 Hz, CH), 2.05 (d, 1H, J = 16.0 Hz, CH), 1.09 (s, 3H, CH_3),1.04 (s, 3H, CH_3).

Anal. Calcd. for $C_{26}H_{25}NO_3$: C, 78.17; H, 6.31; N, 3.51. Found: C, 78.27; H, 6.14; N, 3.37.

3,3-Dimethyl-9-(4-nitrophenyl)-1,2,3,4,9,10-hexahydrobenzo-[*c*]acridine-1-one, (**4l**).

This compound was obtained according to above general procedure; ir (potassium bromide): 3326, 2960, 1594, 1497, 1395, 1262, 1150, 1060, 834, 804, 756, 640 cm^{-1}; ^1H nmr (DMSO-d_6): δ 9.40 (s, 1H, NH), 8.51 (d, 1H, J = 8.8 Hz, ArH), 8.09 (d, 2H, J = 8.4 Hz, ArH), 7.84 (d, 1H, J = 8.0 Hz, ArH), 7.62-7.48 (m, 5H, ArH), 7.27 (d, 1H, J = 8.4 Hz, ArH), 5.41(s, 1H, CH), 2.76 (d, 1H, J = 16.8 Hz, CH), 2.69 (d, 1H, J = 16.8 Hz, CH), 2.26 (d, 1H, J = 16.4 Hz, CH), 2.05 (d, 1H, J = 16.4 Hz, CH), 1.09 (s, 3H, CH_3), 0.98 (s, 3H, CH_3).

Anal. Calcd. for $C_{25}H_{22}N_2O_3$: C, 75.36; H, 5.57; N, 7.03. Found: C, 75.66; H, 5.33; N, 7.21.

3,3-Dimethyl-9-(3-nitrophenyl)-1,2,3,4,9,10-hexahydrobenzo-[*c*]acridine-1-one, (**4m**).

This compound was obtained according to above general procedure; ir (potassium bromide): 3310, 2956, 1589, 1387, 1262, 1150, 1093, 831, 807, 758, 611 cm^{-1}; ^1H nmr (DMSO-d_6):

δ 9.43 (s, 1H, NH), 8.50 (d, 1H, J = 8.4 Hz, ArH), 8.08 (s, 1H, ArH), 7.97-7.95 (dd, 1H, J_1 = 8.4 Hz, J_2 = 1.4 Hz, ArH), 7.74 (d, 1H, J = 7.6 Hz, ArH), 7.72 (d, 1H, J = 7.8 Hz, ArH), 7.61-7.49 (m, 4H, ArH), 7.34 (d, 1H, J = 8.4 Hz, ArH), 5.44 (s, 1H, CH) 2.78 (d, 1H, J = 15.6 Hz, CH), 2.74 (d, 1H, J = 15.6 Hz, CH), 2.27 (d, 1H, J = 16.4 Hz, CH), 2.05 (d, 1H, J = 16.0 Hz, CH), 1.09 (s, 3H, CH_3), 0.99 (s, 3H, CH_3).

Anal. Calcd. for $C_{25}H_{22}N_2O_3$: C, 75.36; H, 5.57; N, 7.03. Found: C, 75.56; H, 5.36; N, 7.15.

3,3-Dimethyl-9-(2-thiophenyl)-1,2,3,4,9,10-hexahydrobenzo-[*c*]acridine-1-one, (**4n**).

This compound was obtained according to above general procedure; ir (potassium bromide): 3320, 2957, 1585, 1518, 1495, 1377, 1260, 1149, 1060, 887, 851, 747, 697 cm^{-1}; ^1H nmr (DMSO-d_6): δ 9.42 (s, 1H, NH), 8.44 (d, 1H, J = 8.8 Hz, ArH), 7.89 (d, 1H, J = 8.4 Hz, ArH), 7.56-7.44 (m, 2H, ArH), 7.35 (d, 1H, J = 5.2 Hz, ArH), 7.24 (s, 1H, ArH), 7.14 (d, 1H, J = 5.2 Hz, ArH), 6.95 (t, 1H, J = 4 Hz, ArH), 6.78-6.76 (m, 1H, ArH), 5.24 (s, 1H, CH) 2.73 (d, 1H, J = 16.8 Hz, CH), 2.62 (d, 1H, J = 16.8 Hz, CH), 2.23 (d, 1H, J = 16.4 Hz, CH), 2.13 (d, 1H, J = 16.4 Hz, CH), 0.97 (s, 3H, CH_3), 0.88 (s, 3H, CH_3).

Anal. Calcd. for $C_{23}H_{21}NOS$: C, 76.85; H, 5.89; N, 3.90; S, 8.92. Found: C, 76.67; H, 5.98; N, 3.78; S, 8.99.

3,3-Dimethyl-9-(*n*-butyl)-1,2,3,4,9,10-hexahydrobenzo[*c*]acridine-1-one, (**4o**).

This compound was obtained according to above general procedure; ir (potassium bromide): 3321, 2953, 1586, 1519, 1495, 1399, 1262, 1151, 1041, 816, 747, 661, 618, 595 cm^{-1}; ^1H nmr (DMSO-d_6): δ 9.03 (s, 1H, NH), 8.40 (d, 1H, J = 8.0 Hz, ArH), 7.86 (d, 1H, J = 8.4 Hz, ArH), 7.55-7.49 (m, 3H, ArH), 7.28 (d, 1H, J = 8.4 Hz, ArH), 4.08 (t, 1H, J = 2.7 Hz, CH), 2.65 (d, 1H, J = 24.2 Hz, CH), 2.54 (d, 1H, J = 24.2 Hz, CH), 2.24 (d, 1H, J = 16.0 Hz, CH), 2.12 (d, 1H, J = 15.6 Hz, CH), 1.60-1.50 (m, 2H, CH), 1.40-1.30 (m, 2H, CH), 1.10 (s, 3H, CH_3), 1.08 (s, 3H, CH_3), 1.00-0.98 (m, 2H, CH), 0.72 (t, 3H, J = 3.5 Hz, CH_3).

Anal. Calcd. for $C_{23}H_{27}NO$: C, 82.84; H, 8.16; N, 4.20. Found: C, 82.66; H, 8.36; N, 4.33.

General Procedure for 3,3-Dimethyl-9-substituted-1,2,3,4,9,10-hexahydrobenzo[*a*]acridine-1-ones (**6**).

A solution of the appropriate aldehyde (2 mmol), dimedone (2 mmol), β-naphthylamine (2 mmol) and in ethanol (3 mL) was irradiated for 4-9 min with power 220 W. The reaction mixture was cooled to room temperature, then poured into water (50 mL), filtered to give the crude product, which was further purified by recrystallization from EtOH (**6a**-**6m**). All products were characterized by IR, ^1H NMR and elemental analysis.

3,3-Dimethyl-9-(4-chlorophenyl)-1,2,3,4,9,10-hexahydrobenzo-[*a*]acridine-1-one, (**6a**).

This compound was obtained according to above general procedure; ir (potassium bromide): 3257, 2935, 1579, 1520, 1493, 1387, 1258, 1150, 1086, 1013, 843, 820, 748, 659 cm^{-1}; ^1H nmr (DMSO-d_6): δ 9.77 (s, 1H, NH), 7.90 (d, 1H, J=8.8 Hz, ArH), 7.82-7.79 (m, 2H, ArH), 7.42 (t, 1H, J=7.6 Hz, ArH), 7.33–7.30 (m, 2H, ArH), 7.24 (d, 2H, J=8.4 Hz, ArH), 7.19 (d, 2H, J=8.4 Hz, ArH), 5.80 (s, 1H, CH), 2.56 (d, 1H, J=16.8 Hz, CH), 2.39 (d, 1H, J=16.8 Hz, CH), 2.23 (d, 1H, J=16.0 Hz, CH), 2.03 (d, 1H, J=16.0 Hz, CH), 1.04 (s, 3H, CH_3), 0.84 (s, 3H, CH_3).

Anal. Calcd. for $C_{25}H_{22}ClNO$: C, 77.41; H, 5.72; N, 3.61. Found: C, 77.65; H, 5.81; N, 3.44.

3,3-Dimethyl-9-(4-bromophenyl)-1,2,3,4,9,10-hexahydrobenzo-[*a*]acridine-1-one, (**6b**).

This compound was obtained according to above general procedure; ir (potassium bromide): 3264, 2927, 1595, 1520, 1493, 1382, 1238, 1146, 1073, 1101, 835, 807, 711, 650 cm^{-1}; ^1H nmr (DMSO-d_6): δ 9.76 (s, 1H, NH), 7.90 (d, 1H, J = 8.4 Hz, ArH), 7.82-7.79 (m, 2H, ArH), 7.42 (t, 1H, J = 7.6 Hz, ArH), 7.34-7.31 (m, 4H, ArH), 7.18 (d, 2H, J = 8.4 Hz, ArH), 5.78 (s, 1H, CH), 2.56 (d, 1H, J = 16.8 Hz, CH), 2.39 (d, 1H, J = 16.8 Hz, CH), 2.23 (d, 1H, J = 16.4 Hz, CH), 2.03 (d, 1H, J = 16.4 Hz, CH), 1.04 (s, 3H, CH_3), 0.84 (s, 3H, CH_3).

Anal. Calcd. for $C_{25}H_{22}BrNO$: C, 69.45; H, 5.13; N, 3.24. Found: C, 69.66; H, 5.24; N, 3.09.

3,3-Dimethyl-9-(4-methoxyphenyl)-1,2,3,4,9,10-hexahydrobenzo-[*a*]acridine-1-one, (**6c**).

This compound was obtained according to above general procedure; ir (potassium bromide): 3269, 2928, 1599, 1520, 1499, 1383, 1259, 1175, 1148, 1033, 811, 746, 678 cm^{-1}; ^1H nmr (DMSO-d_6): δ 9.67 (s, 1H, NH), 7.94 (d, 1H, J = 8.8 Hz, ArH), 7.78 (t, 2H, J = 9.8 Hz, ArH), 7.41 (t, 1H, J = 7.6 Hz, ArH), 7.32-7.28 (m, 2H, ArH), 7.13 (d, 2H, J = 8.4 Hz, ArH), 6.68 (d, 2H, J = 8.8 Hz, ArH), 5.73 (s, 1H, CH), 3.61 (s, 3H, OCH_3), 2.54 (d, 1H, J = 16.4 Hz, CH), 2.38 (d, 1H, J = 16.4 Hz, CH), 2.22 (d, 1H, J = 16.0 Hz, CH), 2.02 (d, 1H, J = 16.0 Hz, CH), 1.03 (s, 3H, CH_3), 0.86 (s, 3H, CH_3).

Anal. Calcd. for $C_{26}H_{25}NO_2$: C, 81.43; H, 6.57; N, 3.65. Found: C, 81.66; H, 6.34; N, 3.54.

3,3-dimethyl-9-(3,4-methylenedioxylphenyl)-1,2,3,4,9,10-hexa-hydrobenzo[*a*]acridine-1-one, (**6d**).

This compound was obtained according to above general procedure; ir (potassium bromide): 3264, 2958, 1583, 1521, 1497, 1431, 1397, 1240, 1148, 1038, 918, 812, 749, 670, 634 cm^{-1}; ^1H nmr (DMSO-d_6): δ 9.70 (s, 1H, NH), 7.95 (d, 1H, J = 8.4 Hz, ArH), 7.79 (t, 2H, J = 8.8 Hz, ArH), 7. 43 (t, 1H, J = 7.6 Hz, ArH), 7.32 (t, 2H, J = 8.0 Hz, ArH), 6. 78 (s, 1H, ArH), 6.67-6.62 (m, 2H, ArH), 5.86 (d, 2H, J = 14.4 Hz, CH), 5.73 (s, 1H, CH), 2.54 (d, 1H, J = 16.8 Hz, CH), 2.40 (d, 1H, J = 16.8 Hz, CH), 2.22 (d, 1H, J = 16.0 Hz, CH), 2.04 (d, 1H, J = 16.0 Hz, CH), 1.04 (s, 3H, CH_3), 0.88 (s, 3H, CH_3).

Anal Calcd. for $C_{26}H_{23}NO_3$: C, 78.57; H, 5.83; N, 3.52. Found: C, 78.66; H, 5.68; N, 3.32.

3,3-Dimethyl-9-(3,4-dimethoxyphenyl)-1,2,3,4,9,10-hexahydro-benzo[*a*]acridine-1-one, (**6e**).

This compound was obtained according to above general procedure; ir (potassium bromide): 3294, 2899, 1602, 1513, 1493, 1417, 1339, 1234, 1137, 1029, 980, 936, 809, 748, 648 cm^{-1}; ^1H nmr (DMSO-d_6): δ 9.68 (s, 1H, NH), 8.00 (d, 1H, J = 8.4 Hz, ArH), 7.81-7.76 (m, 2H, ArH), 7.43 (t, 1H, J = 7.6 Hz, ArH), 7.31 (t, 2H, J = 7.0 Hz, ArH), 6.96 (s, 1H, ArH), 6.67 (d, 1H, J = 8.4 Hz, ArH), 6.58 (dd, 1H, J_1 = 8.2 Hz, J_2 = 1.6 Hz, ArH), 5.74 (s, 1H, CH), 3.63 (s, 3H, OCH_3), 3.60 (s, 3H, OCH_3), 2.55 (d, 1H, J = 16.8 Hz, CH), 2.39 (d, 1H, J = 16.8 Hz, CH), 2.23 (d, 1H, J = 16.0 Hz, CH), 2.05 (d, 1H, J = 16.0 Hz, CH), 1.06 (s, 3H, CH_3), 0.88 (s, 3H, CH_3).

Anal. Calcd. for $C_{27}H_{27}NO_3$: C, 78.42; H, 6.58; N, 3.39. Found: C, 78.56; H, 6.32; N, 3.16.

3,3-Dimethyl-9-(phenyl)-1,2,3,4,9,10-hexahydrobenzo[*a*]acridine-1-one, (**6f**).

This compound was obtained according to above general procedure; ir (potassium bromide): 3236, 2961, 1579, 1520, 1494, 1385, 1261, 1119, 1035, 982, 839, 816, 752, 698, 657 cm^{-1}; ^1H nmr (DMSO-d_6): δ 9.71 (s, 1H, NH), 7.95 (d, 1H, J = 8.4 Hz, ArH), 7.79 (t, 2H, J = 7.6 Hz, ArH), 7.42 (t, 1H, J = 7.6 Hz, ArH), 7.33-7.23 (m, 3H, ArH), 7.12 (t, 2H, J = 7.6 Hz, ArH), 6.99 (t, 2H, J = 7.2 Hz, ArH), 5.79 (s, 1H, CH), 2.55 (d, 1H, J = 16.8 Hz, CH), 2.40 (d, 1H, J = 16.8 Hz, CH), 2.22 (d, 1H, J = 16.0 Hz, CH), 2.02 (d, 1H, J = 16.0 Hz, CH), 1.03 (s, 3H, CH_3), 0.84 (s, 3H, CH_3).

Anal. Calcd. for $C_{25}H_{23}NO$: C, 84.95; H, 6.56; N, 3.96. Found: C, 84.81; H, 6.77; N, 3.73.

3,3-Dimethyl-9-(4-nitrophenyl)-1,2,3,4,9,10-hexahydrobenzo-[*a*]acridine-1-one, (**6g**).

This compound was obtained according to above general procedure; ir (potassium bromide): 3269, 2959, 1602, 1520, 1493, 1383, 1344, 1110, 1014,831, 815, 746, 696 cm^{-1}; ^1H nmr (DMSO-d_6): δ 9.88 (s, 1H, NH), 8.04 (d, 2H, J = 8.8 Hz, ArH), 7.91-7.82 (m, 3H, ArH), 7.51 (d, 2H, J = 8.8 Hz, ArH), 7.44-7.31 (m, 3H, ArH), 5.95 (s, 1H, CH)，2.58 (d, 1H, J = 16.8 Hz, CH), 2.41 (d, 1H, J = 16.8 Hz, CH), 2.25 (d, 1H, J = 16.0 Hz, CH), 2.03 (d, 1H, J = 16.0 Hz, CH), 1.04 (s, 3H, CH_3), 0.82 (s, 3H, CH_3)

Anal. Calcd. for $C_{25}H_{22}N_2O_3$: C, 75.36; H, 5.57; N, 7.03. Found: C, 75.57; H, 5.74; N, 7.13.

3,3-Dimethyl-9-(3-nitrophenyl)-1,2,3,4,9,10-hexahydrobenzo-[*a*]acridine-1-one, (**6h**).

This compound was obtained according to above general procedure; ir (potassium bromide): 3260, 2928, 1582, 1522, 1494, 1385, 1234, 1155, 1093, 982, 923, 811, 729, 687, 654 cm^{-1}; ^1H nmr (DMSO-d_6): δ 9.90 (s, 1H, NH), 8.07 (s, 1H, ArH), 7.96-7.82 (m, 4H, ArH), 7.70 (d, 1H, J = 7.6 Hz, ArH), 7.48-7.31 (m, 4H, ArH), 5.97 (s, 1H, CH)，2.58 (d, 1H, J = 16.4 Hz, CH), 2.43 (d, 1H, J = 16.4 Hz, CH), 2.25 (d, 1H, J = 16.0 Hz, CH), 2.04 (d, 1H, J = 16.0 Hz, CH), 1.06 (s, 3H, CH_3), 0.82 (s, 3H, CH_3).

Anal. Calcd. for $C_{25}H_{22}N_2O_3$: C, 75.36; H, 5.57; N, 7.03. Found: C, 75.57; H, 5.73; N, 7.17.

3,3-Dimethyl-9-(4-hydroxy-3-methoxyphenyl)-1,2,3,4,9,10-hexa-hydrobenzo[*a*]acridine-1-one, (**6i**).

This compound was obtained according to above general procedure; ir (potassium bromide): 3267, 2958, 1602, 1511, 1497, 1427, 1399, 1272, 1149, 1034, 979, 857, 748, 630 cm^{-1}; ^1H nmr (DMSO-d_6): δ 9.64 (s, 1H, NH), 8.61 (s, 1H, OH), 8.00 (d, 1H, J = 8.4 Hz, ArH), 7.81-7.75 (m, 2H, ArH), 7.43 (t, 1H, J = 7.6 Hz, ArH), 7.33-7.28 (m, 2H, ArH), 6.92 (s, 1H, ArH), 6.47 (t, 2H, J = 9.6 Hz, ArH), 5.70 (s, 1H, CH), 3.64 (s, 3H, OCH_3), 2.55(d, 1H, J = 16.4 Hz, CH), 2.38 (d, 1H, J = 16.4 Hz, CH), 2.22 (d, 1H, J = 16.0 Hz, CH), 2.04 (d, 1H, J = 16.0 Hz, CH), 1.06 (s, 3H, CH_3), 0.88 (s, 3H, CH_3).

Anal. Calcd. for $C_{26}H_{25}NO_3$: C, 78.17; H, 6.31; N, 3.51. Found: C, 78.35; H, 6.55; N, 3.24.

3,3-Dimethyl-9-(2-thiophenyl)-1,2,3,4,9,10-hexahydrobenzo[*a*]-acridine-1-one, (**6j**).

This compound was obtained according to above general procedure; ir (potassium bromide): 3266, 2927, 1600, 1521, 1493, 1379, 1235, 1184, 1032, 978, 812, 746, 693 cm^{-1}; ^1H nmr (DMSO-d_6): δ 9.83 (s, 1H, NH), 8.00 (d, 1H, J = 8.8 Hz, ArH), 7.85-7.80 (m, 2H, ArH), 7.49 (t, 1H, J = 7.6 Hz, ArH), 7.38-7.28 (m, 2H, ArH), 7.11 (d, 1H, J = 4.8 Hz, ArH), 6.72 (t, 1H, J = 4.4 Hz, ArH), 6.60 (d, 1H, J = 3.2 Hz, ArH), 6.12 (s, 1H, CH), 2.56 (d, 1H, J = 16.8 Hz, CH), 2.41 (d, 1H, J = 16.8 Hz, CH), 2.27 (d, 1H, J = 16.0 Hz, CH), 2.11 (d, 1H, J = 16.0 Hz, CH), 1.06 (s, 3H, CH_3), 0.95 (s, 3H, CH_3).

Anal. Calcd. for $C_{23}H_{21}NOS$: C, 76.85; H, 5.89; N, 3.90; S, 8.92. Found: C, 76.67; H, 5.76; N, 3.79; S, 8.67.

3,3-Dimethyl-9-[4-(1,3-benzoxazol-2-yl)phenyl]-1,2,3,4,9,10-hexahydrobenzo[*a*]acridine-1-one, (**6k**).

This compound was obtained according to above general procedure; ir (potassium bromide): 3261, 2954, 1601, 1523, 1499, 1471, 1399, 1243, 1170, 1149, 1016, 816, 745, 660 cm^{-1}; ^1H nmr (DMSO-d_6): δ 9.84 (s, 1H, NH), 8.01-7.95 (m, 3H, ArH), 7.84-7.73 (m, 4H, ArH), 7.49-7.32 (m, 7H, ArH), 5.91 (s, 1H, CH), 2.59 (d, 1H, J = 16.8 Hz, CH), 2.43 (d, 1H, J = 16.8 Hz, CH), 2.25 (d, 1H, J = 16.0 Hz, CH), 2.07 (d, 1H, J = 16.0 Hz, CH), 1.05 (s, 3H, CH_3), 0.85 (s, 3H, CH_3).

Anal. Calcd. for $C_{32}H_{26}N_2O_2$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.85; H, 5.78; N, 5.89.

3,3-Dimethyl-9-(1*H*-indol-3-yl)-1,2,3,4,9,10-hexahydrobenzo-[*a*]acridine-1-one, (**6l**).

This compound was obtained according to above general procedure; ir (potassium bromide): 3268, 2924, 1569, 1519, 1500, 1467, 1351, 1240, 1154, 1093, 1031, 813, 732, 656 cm^{-1}; ^1H nmr (DMSO-d_6): δ 10.65 (s, 1H, NH), 9.77 (s, 1H, NH), 8.12 (d, 1H, J = 8.4 Hz, ArH), 7.73 (t, 2H, J = 9.2 Hz, ArH), 7.54 (d, 1H, J = 7.6 Hz, ArH), 7.38-7.08 (m, 5H, ArH), 6.90 (t, 1H, J = 7.6 Hz, ArH), 6.80 (t, 1H, J = 7.6 Hz, ArH), 6.08 (s, 1H, CH), 2.54 (d, 1H, J = 16.4 Hz, CH), 2.40 (d, 1H, J = 16.4 Hz, CH), 2.19 (d, 1H, J = 16.0 Hz, CH), 1.98 (d, 1H, J = 16.0 Hz, CH), 1.02 (s, 3H, CH_3), 0.77 (s, 3H, CH_3).

Anal. Calcd. for $C_{27}H_{24}N_2O$: C, 82.62; H, 6.16; N, 7.14. Found: C, 82.88; H, 6.09; N, 7.21.

3,3-Dimethyl-9-(*n*-butyl)-1,2,3,4,9,10-hexahydrobenzo[*a*]acri–dine-1-one, (**6m**).

This compound was obtained according to above general procedure; ir (potassium bromide): 3280, 2952, 1596, 1521, 1491, 1399, 1262, 1151, 1128, 818, 749, 709, 661 cm^{-1}; ^1H nmr (DMSO-d_6): δ 9.40 (s, 1H, NH), 7.98 (d, 1H, J=8.4 Hz, ArH), 7.82 (d, 1H, J=8.0 Hz, ArH), 7.71 (d, 1H, J=8.8 Hz, ArH), 7.51 (t, 1H, J=7.6 Hz, ArH), 7.35 (t, 1H, J=7.6 Hz, ArH), 7.18 (d, 1H, J=8.8 Hz, ArH), 4.78 (t, 1H, J= 4.8 Hz, CH), 2.50 (d, 1H, J=16.8 Hz, CH), 2.39 (d, 1H, J=16.8 Hz, CH), 2.23 (d, 1H, J=16.0 Hz, CH), 2.15 (d, 1H, J=16.0 Hz, CH), 1.53-1.43 (m, 2H, CH), 1.24-1.14 (m, 2H, CH), 1.11 (s, 3H, CH_3), 1.07 (s, 3H, CH_3), 0.99-0.90 (m, 2H, CH), 0.68 (t, 3H, J= 7.2 Hz, CH_3).

Anal. Calcd. for $C_{23}H_{27}NO$: C, 82.84; H, 8.16; N, 4.20. Found: C, 82.99; H, 8.23; N, 4.31.

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[13] The single-crystal growth was carried out in ethanol at room temperature. X-ray crystallographic analysis was performed with a Siemens SMART CCD and a Siemens P4 diffractometer. Crystal data for **6b**: $C_{25}H_{22}BrNO$, yellow, crystal dimension 0.32 x 0.27 x 0.09 mm, Triclinic, space group P-1, a= 7.296(4), b = 9.597(5), c = 15.304(8) Å, α = 94.038(7)°, β = 93.465(8)°, γ = 103.331(7)°, V = 1036.9(9) Å^3, Mr = 432.35, Z = 2, Dc = 1.385 g/cm^3, λ = 0.71073 Å, μ ($Mok\alpha$) = 1.997 mm^{-1}, $F(000)$ = 444, S =1.008, R_1= 0.0442, $wR2$ = 0.0999.