Intermediates for the Synthesis of Indole Alkaloids. Synthesis of Tetrahydrocarbazole Derivatives

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The synthesis of new precursors **8** and **15** for the synthesis of tetracyclic indole alkaloids were described. Many new intermediates **4-7** and **9-14** have also been synthesized.

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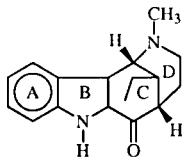
Tetrahydrocarbazole derivatives have an important role in the synthesis of indole alkaloids [1,2,3]. The carbonyl functionality at the C-4 position allows construction of the D ring of the tetracyclic skeleton. Reported methods for this conversion fall into three different strategies all of which include an intramolecular cyclization leading to formation of the D ring. The first method was a 2-substituted 4-acetaminohexahydrocarbazole as the starting material for ring formation [1]. Similarly, tetrahydrocarbazole-2-acetic acid derivatives were used in the second method [2]. Aldol condensation of 1-oxo-4-aminotetrahydrocarbazole derivatives is in the scope of the third method [3].

In the present work, the synthesis of 2-ethyl-substituted tetrahydrocarbazole derivatives are described. These intermediates such as **8** and **15** could be useful starting materials for the synthesis of the indole alkaloids dasycarpidone (**1**) and uleine (**2**).



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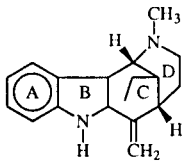

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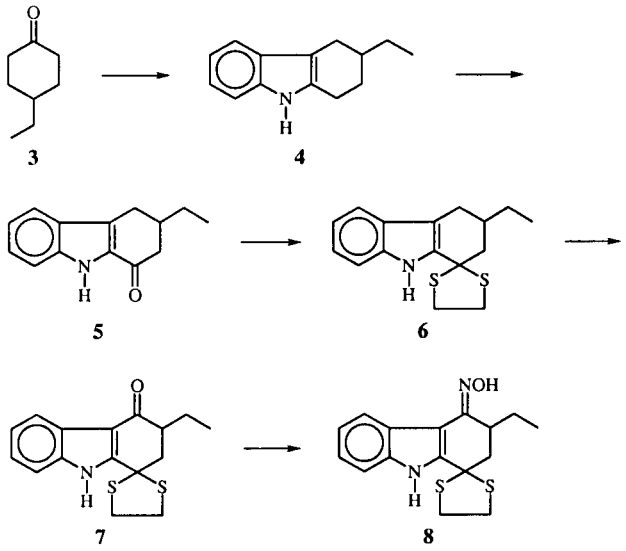
Scheme 1 outlines the synthesis of intermediate **8**. In the first step, a successful Fischer-Indole synthesis commencing with 4-ethylcyclohexanone led to the formation of compound **4** [4]. Oxidation of this intermediate with periodic acid resulted in the formation of compound **5** which in the next step was protected with ethanedithiole to give **6** [5,6]. Finally, compound **7** was obtained after a succesful oxidation step with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone at position 4 of compound **6** [7]. After that, compound **8** was optained from **7** with hydroxylamine hydrochloride in propanol [8].

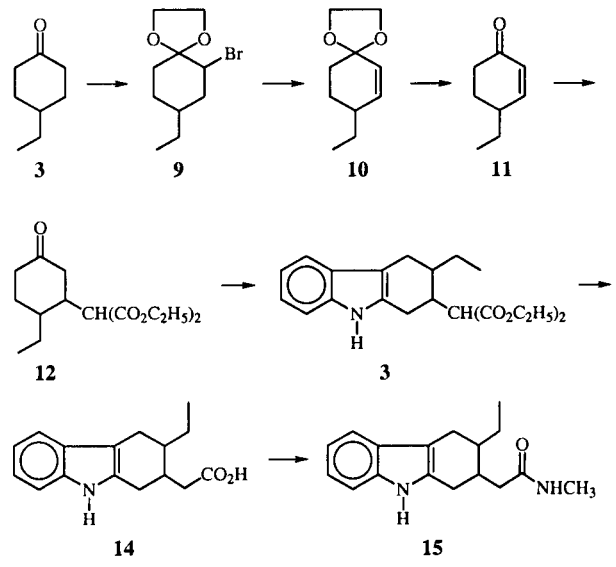
Synthesis of 2-substituted-3-ethyltetrahydrocarbazoles are outlined in Scheme 2. A Fischer-indole reaction of compound **12** gave the desired intermediate **13**. In turn, synthesis of compound **12** was achieved by using 4-ethyl-2-cyclohexenone as the starting material for a successful Michael reaction [9]. The yield of this conversion was found to be higher than the yields reported in the literature [10].

Scheme 1



Reaction of 4-ethylcyclohexanone with ethylene glycol and bromine gave compound **9** which in turn was subjected to an elimination reaction to give compound **10**. Acidic hydrolysis of the ketal functionality resulted in formation of

Scheme 2



compound **11** in good yield [11]. Ester hydrolysis of **13** and subsequent decarboxylation led to the formation of compound **14** which was converted to its *N*-methylamide derivative **15** in the next step [9, 2].

EXPERIMENTAL

All melting points were measured in sealed tubes using an electrothermal digital melting points apparatus (Gallenkamp) and are uncorrected. Mass spectra were recorded on a HP 5971 mass and combined 5980 gas chromatography system. Infrared spectra were recorded on Hitachi 270-30 infrared spectrometer. The ^{1}H-nmr spectra were obtained on a high resolution fourier transform 400 MHz Bruker WH and 200 MHz Gemini Varian NMR spectrometers with tetramethylsilane as an internal standard. Analytical and preperative thin layer chromatography (tlc) were performed on silica gel 60 PF254 (Merck). Column chromatography was carried out by using 70-230 mesh silica gel (0.063-0.2 mm, Merck).

3-Ethyl-1,2,3,4-tetrahydrocarbazole (**4**).

A solution of 12.60 g (100 mmoles) of 4-ethylcyclohexanone, 15.90 g of phenylhydrazine hydrochloride (110 mmoles) and 100 ml of ethanol was refluxed for 5 hours under nitrogen. The mixture was allowed to cool to room temperature and then concentrated on a rotary evaporator. The crude product was dissolved in chloroform and washed first with 50 ml of 10% hydrochloric acid and then with 50 ml of 10% sodium carbonate solutions. The organic layer was dried over anhydrous magnesium sulfate and the solvent was evaporated on a rotary evaporator. The residue was dissolved in benzene and chromatographed on silica gel using benzene to yield 15.6 g. (78%) of **4** as a solid, rf: 0.62 (benzene); mp 124°; ir (potassium bromide): ν 3420 (NH), 2980 (CH) cm^{-1}; ms: (m/z) 199 (48), 168 (13), 143 (100), 130 (8), 115 (9); ^{1}H nmr (deuteriochloroform): δ 1.05 (t, 3H, CH_2CH_3), 1.50 (q, 2H, CH_2CH_3), 1.55 (m, 1H, CH), 1.75 (m, 1H, CH), 2.05 (m, 1H, CH), 2.30 (m, 1H, CH), 2.75 (m, 2H, CH_2), 2.90 (dd, 1H, CH), 7.05-7.15 (m, 2H, aromatic protons), 7.25-7.30 (m, 1H, aromatic proton), 7.48-7.52 (m, 1H, aromatic proton), 7.65 (bs, 1H, N-H).

Anal. Calcd. for $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.26; H, 8.56; N, 6.98.

3-Ethyl-1,2,3,4-tetrahydrocarbazol-1-one (**5**).

To a solution of 12.54 g (55 mmoles) periodic acid in 100 ml of methanol-water (1:1) was added dropwise 5.47 g (27.5 mmoles) of **4** in 25 ml of methanol at 0°. The reaction mixture was stirred for 1 hour at 0°, then stirring was continued for one more hour at room temparature. The solvent was evaporated then the residue was dissolved in chloroform and first washed with 50 ml of 10% sodium carbonate and then with 50 ml of 10% sodium bisulfide. The organic layer was dried over anhydrous magnesium sulfate and the solvent was evaporated. Recrystallization of the residue from cyclohexane yielded 5.15 g (88%) of **5**, rf: 0.56 (ethyl acetate); mp 143-144°; ir (potassium bromide): ν 3270 (NH), 2920 (CH), 1650 (C=O) cm^{-1}; ms: (m/z) 213 (100), 184 (7), 156 (33), 129 (98); ^{1}H nmr (deuteriochloroform): δ 1.1 (t, 3H, CH_2CH_3), 1.5-1.62 (m, 2H, CH_2CH_3), 2.21-2.38 (m, 1H, CH), 2.40-2.48 (m, 1H, CH), 2.58-2.65 (m, 1H, CH), 2.66-2.78 (m, 1H, CH), 3.18-3.22 (m, 1H, CH), 7.10-7.15 (m, 1H, aromatic proton), 7.32-7.38 (m, 1H, aromatic proton), 7.39-7.43 (m, 1H, aromatic proton), 7.62-7.65 (m, 1H, aromatic proton), 9.22 (s, 1H, NH).

Anal. Calcd. for $C_{14}H_{15}NO$: C, 78.87; H, 7.04; N, 6.57. Found: C, 78.83; H, 6.96; N, 6.61.

3-Ethyl-2,3,4,9-tetrahydrospiro[1*H*-carbazole-1,2'-(1,3)dithiolane] (**6**).

To a solution of 5 g (23.47 mmoles) of **5** in 50 ml of dichloromethane was added 3.84 g (28.17 mmoles) of zinc chloride and 2.65 g (28.17 mmoles) of 1,2-ethanedithiol. The mixture was refluxed for 3 hours, then the reaction mixture was washed with 50 ml of 20% potassium hydroxide. The organic layer was dried over anhydrous magnesium sulfate and the solvent was evaporated. Recrystallization of the product from cyclohexane yielded 6 g (88%) of **6**, rf: 0.43 (benzene), mp 112-113°; ir (potassium bromide): ν 3380 (NH), 2920 (CH) cm^{-1}; ms: (m/z) 289 (52), 261 (10), 229 (25), 200 (47), 180 (14), 167 (100), 129 (13); ^{1}H nmr (deuteriochloroform): δ 1.5 (t, 3H, CH_2CH_3), 1.51-1.62 (m, 2H, CH_2CH_3), 2.05-2.18 (m, 1H), 2.20-2.38 (m, 2H), 2.51-2.58 (m, 1H), 2.91-2.98 (m, 1H), 3.38-3.76 (m, 4H, SCH_2CH_2S), 7.04-7.08 (m, 1H, aromatic proton), 7.16-7.20 (m, 1H, aromatic proton), 7.25-7.34 (m, 1H, aromatic proton), 7.48-7.56 (m, 1H, aromatic proton), 8.21 (s, 1H, N-H).

Anal. Calcd. for $C_{16}H_{19}NS_2$: C, 64.44; H, 6.57; N, 4.84. Found: C, 64.41;H, 6.59; N, 4.79.

3-Ethyl-2,3,4,9-tetrahydrospiro[1*H*-carbazole-1,2'-(1,3)-dithiolane]-4-one (**7**).

To a solution of 9.43 g (32.63 mmoles) of **6** in 50 ml of tetrahydrofurane (90%) was added dropwise 4.81 g (65.26 mmoles) of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone in tetrahydrofurane at 0°. The reaction mixture was stirred for 5 hours at room temperature, then the solution was poured into 500 ml of 10% solution of sodium hydroxide and extracted twice with ethyl acetate. The organic layer was dried with anhydrous magnesium sulfate and the solvent was evaporated. The residue was purified by chromatography using silica gel ethyl acetate to afford 9.12 g (92%) of **7**, rf: 0.67 (ethyl acetate), mp 181-182°; ir (potassium bromide): ν 3220 (NH), 2920 (CH), 1630 (C=O) cm^{-1}; ms: (m/z) 303.1 (100), 275 (75), 242 (81), 228 (36), 215 (70), 185.1 (45), 167 (39), 159 (50); ^{1}H nmr (deuteriochloroform): δ 1.1 (t, 3H, CH_2CH_3), 1.62-1.75 (m, 1H); 2.08-2.18, (m, 1H), 2.64-2.78 (m, 2H, CH_2CH_3), 2.84-2.96 (m, 1H), 3.42-3.76.(m, 4H, SCH_2CH_2S), 7.20-7.37 (m, 3H, aromatic protons), 8.21-8.27 (m, 1H, aromatic proton), 8.86 (s, 1H, NH).

Anal. Calcd. for $C_{16}H_{17}NS_2O$: C, 63.37; H, 5.61; N, 4.62. Found: C, 63.41; H, 5.58; N, 4.68.

3-Ethyl-2,3,4,9-tetrahydrospiro[1*H*-carbazole-1,2'-(1,3)-dithiolane]-4-one Oxime (**8**).

To a solution of 0.5 g (1.6 mmoles) of **7** in 25 ml of propanol was added 1.72 g (24.7 mmoles) of hydroxyl amine hydrochloride and 2.02 g (24.7 mmoles) of sodium acetate in 10 ml of water. The reaction mixture was refluxed for 96 hours, then the reaction mixture was poured into 50 ml of 10% sodium carbonate and extracted with ethyl acetate. The organic layer was dried over anhydrous magnesium sulfate and the solvent was evaporated. The residue was chromatographed using silica gel and ethyl acetate *n*-hexane (1:1). After crystallization from diethyl ether *n*-hexane yielded 0.25 g (48%) of **8**, rf; 0.61 (ethyl acetate-hexane (1:1)), mp: 91-93°; ir (potassium bromide): ν 3400 (OH), 3320 (NH), 2900 (CH), 1620 (C=N) cm^{-1}; ms: (m/z) 318 (0.2), 282 (1.5), 279 (1.30), 167 (6), 149 (43), 113 (11), 97 (12), 85 (71), 83 (100), 69 (45), 59 (76), 43 (100), 31 (91); ^{1}H nmr (deuteriochloroform): δ 1.01-1.07 (t, 3H,

CH_3), 1.40-1.58 (m, 2H), 2.68-2.73 (m, 2H), 3.40-3.50 (m, 4H), 3.52-3.58 (m, 1H), 7.01-7.46 (m, 4H, aromatic protons), 8.37 (s, 1H, NH), 8.38 (s, 1H, OH).

Anal. Calcd. for $C_{16}H_{18}N_2S_2O$: C, 60.35; H, 5.70; N, 8.79. Found: C, 60.38; H, 5.50; N, 8.80.

2-Bromo-4-ethylcyclohexanone Ethylene Ketal (**9**).

To a solution of 12.60 g (100 mmoles) of 4-ethylcyclohexanone in 100 ml of dried ethylene glycol was added dropwise 16 g of bromine at room temparature. The reaction was stopped when no change in the colour of bromine was observed. The mixture was poured into 250 ml of hexane containing 20 g of sodium carbonate slowly. An excess amount of water was added and then the mixture was extracted. The organic layer was dried over anhydrous magnesium sulfate and the solvent was evaporated. Distillation of the product gave 19.42 g (78%) of **9**, bp 165° (5 mm Hg); ir (potassium bromide): ν 2940 (CH), 1150 (C-O-C) cm^{-1}; ms: (m/z) 250 (1.5), 248 (1), 169 (27), 99 (100), 86 (25), 55 (33); ^1H nmr (deuteriochloroform): δ 0.86 (t, 3H, CH_3, J = 6.8 Hz), 1.16-1.94 (m, 8H, CH_2), 2.20-2.31 (m, 1H, CH), 3.99-4.21 (m, 5H, OCH_2CH_2O, CHBr).

Anal. Calcd. for $C_{10}H_{17}O_2Br$: C,48.21; H, 6.88. Found: C, 48.17; H, 6.85.

4-Ethyl-2-cyclohexenone Ethylene Ketal (**10**).

A solution of 24.9 g (100 mmoles) of 2-bromo-4-ethylcyclohexanone ethylene ketal, 100 ml of dimethyl sulfoxide and 16.2 g (300 mmoles) of sodium methoxide was stirred for 4 hours at 80°. Then it was poured into 250 ml water and extracted with *n*-hexane. The organic layer was dried over anhydrous magnesium sulfate and evaporated. Distillation of the residue under vacum afforded 13.27 g (79%) of **10**, bp 130° (5 mm Hg); ir (potassium bromide): ν 2940 (CH), 1100 (C-O-C) cm^{-1}; ms: (m/z) 168 (36), 112 (54), 96 (42), 83 (100), 55 (66), 41 (43); ^1H nmr (deuteriochloroform): δ 0.88 (t, 3H, CH_3), 1.16-1.99 (m, 7H, 2 x CH_2 ring and CH_2CH), 3.82-4.15 (m, 4H, OCH_2CH_2O), 5.51 (dd, 1H, C=CH, J = 10.15 and 1.4 Hz), 5.84 (dd, 1H, C=CH, J:10.15 and 1.4 Hz).

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.37; H, 9.57.

4-Ethyl-2-cyclohexen-1-one (**11**).

A mixture of 10 g (59.52 mmoles) of 4-ethyl-2-cyclohexenone ethylene ketal in 50 ml of dioxane and 50 ml of 5% sulfuric acid was stirred for 30 minutes at room temperature. Then the mixture was extracted with ether and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by vacum distillation gave 5.5 g (74%) of **11**, bp 79° (10 mm Hg) (lit [10] bp 77-80° at 11 mm Hg); ir (potassium bromide): ν 2940 (CH), 1685 (C=O) cm^{-1}; ms: (m/z) 124 (70), 98 (68), 81 (100), 67 (62), 55 (26), 39 (42); ^1H nmr (deuteriochloroform): δ 0.90-1.05 (t, 3H, CH_3), 1.20-2.10 (m, 7H, 2 x CH_2 ring and CH_2CH), 5.95-6.05 (dd, 1H, C=CH, J = 10.08 and 1.35 Hz), 6.55-6.90 (dd, 1H, C=CH, J = 10.08 and 1.35 Hz).

Anal. Calcd. for $C_8H_{12}O$: C,77.38; H, 9.74. Found: C, 77.26; H, 9.69.

Diethyl (4-Ethylcyclohexanon-3-yl)malonate (**12**).

To a solution of a catalytic amount of sodium ethylate in ethanol (prepared by adding 1 g of metallic sodium into 100 ml of absolute ethanol at 0°) was added 8 g (50 mmoles) of diethyl malonate and the solution was stirred for 15 minutes at 0°. To this solution was added dropwise 6.20 g (50 mmoles) of 4-ethyl-2-cyclohexen-1-one at 0°. The solution was allowed to cool to room temperature and stirred for 16 hours. The solution was acidified by adding acetic acid, then diluted with water. It was extracted three times with ether and dried over anhydrous magnesium sulfate. Evaporation of the solvent and distillation of the residue gave 13.5 g (95%) of **12**, bp: 175-177° (5 mm Hg); ir (potassium bromide): ν 2940 (CH), 1740 (C=O), 1650 (C=O) cm^{-1}; ms: (m/z) 256 (2), 225 (15), 168 (20), 153 (66), 125 (100), 55 (49); ^1H nmr (deuteriochloroform): δ 0.80-1.11 (t, 3H, CH_2CH_3), 1.12-1.59 (t, 6H, 2 x OCH_2CH_3), 1.63-2.56 (m, 7H, 2 x CH_2 ring, CH_2CH_3 and $CHCH_2CH_3$ ring), 3.05-3.42 (m, 2H, CH_2 ring), 3.58-3.73 (m, 6H, 2xOCH_2CH_3, $CH(CO_2C_2H_5)_2$ and CH ring).

Anal. Calcd. for $C_{15}H_{24}O_5$: C, 63.35; H, 8.51. Found: C, 63.26; H, 8.48.

(3-Ethyl-1,2,3,4-tetrahydrocarbazole-2-yl)-malonic Acid Diethyl Ester (**13**).

A mixture of 7.1 g (25 mmoles) of **12** and 3.97 g (27.5 mmoles) of phenylhydrazine hydrochloride and in 50 ml of absolute ethanol was refluxed for 5 hours under nitrogen atmosphere and then cooled to room temperature. The solvent was evaporated and the residue was dissolved in chloroform and first washed with 100 ml of 10% hydrochloric acid, then with 100 ml of 10% sodium carbonate. The organic phase was dried over anhydrous magnesium sulfate and the solvent was evaporated. The crude product was dissolved in chloroform and chromatographed using silica gel and ethyl acetate-benzene (4:1) yields 6.90 g (77%) of **13** as an oil, rf: 0.63 (ethyl acetate-benzene, 4:1): ir (potassium bromide): ν 3410 (NH), 2930 (CH), 1750 (C=O), 1730 (C=O) cm^{-1}; ms: (m/z) 357 (80), 312 (26), 255 (62), 210 (17), 182 (23), 130 (42), 117 (22); ^1H nmr (deuteriochloroform): δ 0.93-1.18 (t, 3H, CH_2CH_3), 1.22-1.62 (t, 6H, 2 x OCH_2CH_3), 2.20-3.02 (m, 6H, 2 x CH_2 and 2 x CH ring), 3.41-3.64 (m, 2H, CH_2CH_3), 3.63-3.83 (m, 3H, OCH_2CH_3 and $CH(CO_2C_2H_5)_2$), 4.11-4.28 (q, 2H, OCH_2CH_3), 7.06-7.58 (m, 4H, aromatic protons), 7.85 (broad s, 1H, NH).

Anal. Calcd. for $C_{21}H_{27}NO_4$: C, 70.56; H, 7.61; N, 3.92. Found: C, 70.48; H, 7.59; N, 3.90.

(3-Ethyl-1,2,3,4-tetrahydrocarbazole-2-yl)-acetic Acid (**14**).

A solution of 5 g (14 mmoles) of **13** and 50 ml 20% potassium hydroxide (methanol-water (4:1)) was stirred for 4 hours. The solution was cooled to room temperature and the solvent was evaporated. The residue was cooled to 0° and acidified slowly with 50 ml of 10% hydrochloric acid. The mixture was extracted with ethyl acetate and the organic layer was dried with anhydrous magnesium sulfate. After evaporation of the solvent, the product was heated under vacum (40-50 mmHg) for 30 minutes at 170 yielded 2.5 g (69%) of **14** as an oil, rf: 0.34 (ethyl acetate); ir (potassium bromide): ν 3420 (NH), 3150 (OH), 2930 (CH), 1705 (C=O) cm^{-1}; ms: (m/z) 257 (42), 240 (100), 212 (17), 198 (28), 169 (21); ^1H nmr (deuteriochloroform): δ 0.98-1.05 (t, 3H, CH_2CH_3), 1.50-1.57 (m, 3H, CH_2CH_3 and CH), 2.05-2.30 (m, 2H, CH_2), 2.36-2.47 (m, 1H, CH), 2.63-2.78 (m, 2H, CH_2), 2.80-2.90 (m, 2H, CH_2), 7.05-7.17 (m, 2H, aromatic protons), 7.24-7.32 (d, 1H, aromatic proton), 7.42-7.50 (d, 1H, aromatic proton), 7.92 (s, 1H, NH).

Anal. Calcd. for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N,5.43. Found: C, 74.31; H, 7.22; N, 5.39.

(3-Ethyl-1,2,3,4-tetrahydrocarbazole-2-yl)-*N*-methylacetamide (**15**).

To a solution of 2.11 g (19.45 mmoles) of ethyl of chloroformate in 10 ml chloroform at 0° was added dropwise a solution of 5 g (19.45 mmoles) of **14** followed by 3.93 g (38.91 mmoles) of triethylamine in chloroform. The solution was stirred for 1 hour at 0° and quenched with 10 ml of 60% aqueous methylamine and then the solution was cooled to room temperature. The solution was washed successively with 50 ml of 10% hydrochloric acid and 50 ml of 10% sodium carbonate. The organic layer was dried with anhydrous magnesium sulfate and the solvent was evaporated. Column chromatography using silica gel and ethyl acetate yielded 3 g (57%) of **15**, rf: 0.63 (ethyl acetate); mp 179-180°; ir (potassium bromide): ν 3380 (N-H), 3290 (NH), 2920 (CH), 1655 (C=O) cm^{-1}; ms: (m/z) 270 (19), 256 (57), 240 (72), 226 (18),197 (32), 143 (100), 117 (20); ^1H nmr (deuteriochloroform): δ 1.05 (t, 3H, CH_2CH_3, J = 7.35 Hz), 1.22-1.62 (m, 4H, 2xCH_2 ring), 2.26-2.31 (m, 1H, C*H*), 2.67-2.74 (dd, 1H, *H*CH-C=O, J = 4.65 and 16.70 Hz), 2.80-2.99 (m, 5H, NHC*H*$_3$, C*H*, HC*H*-C=O, J = 4.65 and 16.70 Hz), 3.33 (q, 2H, CH_2CH_3, J = 7.35 Hz), 6.83 (broad s, 1H, N*H*CH_3), 7.09-7.59 (m, 4H, aromatic protons), 8.23 (s,1H, NH).

Anal. Calcd. for $C_{17}H_{22}N_2O$: C, 75.55; H, 8.15; N, 10.37. Found: C, 75.52; H, 8.05; N, 10.45.

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