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4-Piperidone – A synthon for spiro-heterocycles

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A new class of spiro compounds piperidino-oxirane, -cyclopropane, -thiazolidone, -thiadiazole and -thiazine have been developed from tetra substituted 4-piperidone adopting modern synthetic methodologies.

Keywords: 4-Piperidone, microwave, ultrasound, spiro piperidino-oxirane, piperidino-cyclopropane, piperidino-thiazolidone, piperidino-thiadiazole, piperidino-thiazine

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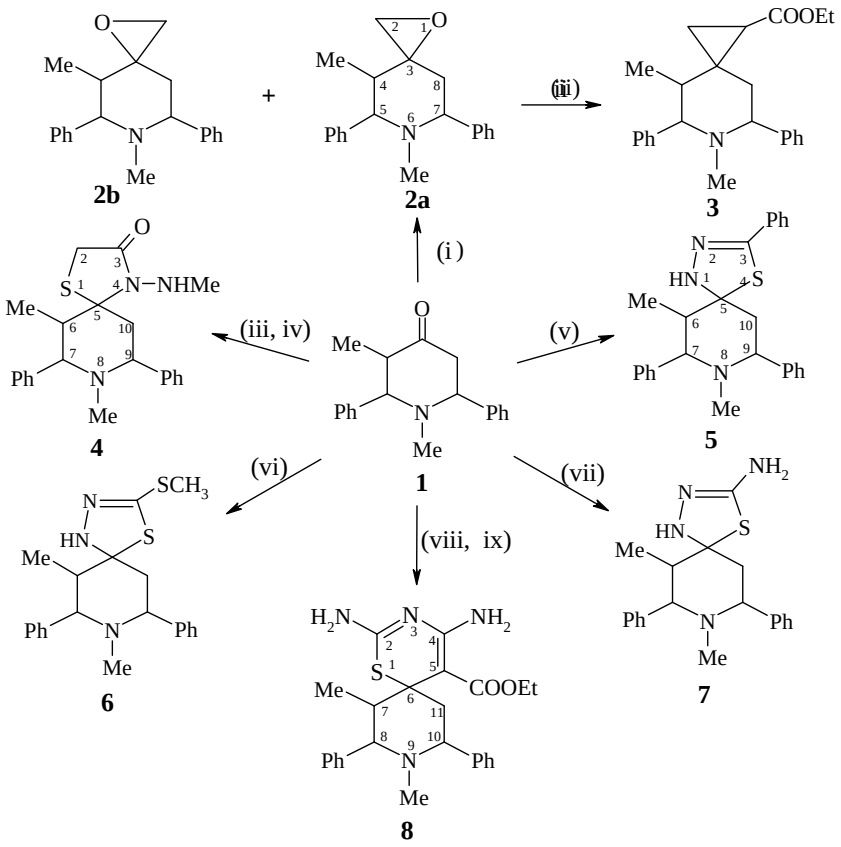
In recent years there has been a great deal of interest in exploring proximal functional groups for designing novel structures capable of performing a variety of functions. One such class of compounds constitute 4-piperidone and their derivatives whose syntheses and stereodynamics are well investigated[1]. In fact, substituted piperidones are the constituents of a variety of alkaloids which possess a broad spectrum of biological activity[2]. Inspite of these extensive studies there is still a scope for exploring the utility of 4-piperidones as synthons for a variety of compounds. In general, an in-built spiro system in heterocyclic ring increases the biological potency and more so with such systems having smaller rings. In fact, heteroatoms in small rings affect bond angles, bond lengths and bond strengths through a combination of factors including their intrinsic hybridization, magnitude of covalent radii, angle-bending constants, non-bonded interactions and long-range electronic effects.

The main objective of the present paper is to study the reactivity of 1,3-dimethyl- 2,6-diphenylpiperidin-4-one **1** by functionalization of carbonyl group in **1** to develop various spiro compounds *viz*., piperidino-oxirane, -cyclopropane, -thiazolidone, -thiadiazole and -thiazine. To accelerate the various reactions and to modernize classical procedures, microwave irradiation and ultrasound techniques were employed. The approach on coupling of microwaves[3] and ultrasound[4] with conventional methods proved to be viable for various types of reactions as there are many obvious advantages *viz*., less reaction time, avoiding the side reactions, better yield and ease of the isolation of products *etc*.

Results and Discussion

Cycloaddition of dimethylsulfoxonium methylide[5] to carbonyl moiety of **1** in the presence of $KOBu^t$ in dry DMSO under ultrasonication resulted in the formation of isomers of 4,6-dimethyl-5,7-diphenyl-1-oxa-6-azaspiro[2.5]octane **2**. They were separated by column chromatography and identified as one with equatorial oxygen **2a** (58%) and the other with axial oxygen **2b** (15%). However, cycloaddition of diazomethane to *cis*-1-methyl-2,6-diaryl-4-piperidones gave the corresponding oxiranes stereoselectively[6] (**Scheme I** and **Table I**). The methine (C-4, C-5, C-7) and methylene (C-8) protons of piperidine ring in **2a** and **2b** in their ^{1}H NMR spectra displayed a doublet at δ 3.27 and 3.25 (C_5-H_{ax}), a multiplet at δ 2.41-2.56 and 2.38-2.54 (C_4-H and C_8-H_{ax}), a double doublet at δ 3.52 and 3.54 (C_7-H_{ax}) and another double doublet at δ 2.13 and 2.10 (C_8-H_{eq}), respectively. The methyl protons at C-4 showed a doublet at δ 0.62 in **2a**, whereas at 1.13 ppm in **2b**. The downfield shift of methyl protons in **2b** confirms that the methyl group and oxygen are in the same plane and also in close proximity with each other. The methylene protons of the oxirane ring (C_2-H) exhibited two doublets at δ 2.68 and 2.65 and 2.89 and 2.91 in **2a** and **2b**, respectively. The compound **2a** on treatment with



(i) TMSOI / $KOBu^t$ / DMSO, US

(ii) $(EtO)_2P(O)CH_2COOEt$ / $KOBu^t$ / DMSO, 65 - 70°C, US

(iii) $MeNHNH_2$ / Ethanol, Δ (iv) $HSCH_2COOH$ / Et_3N / DMF, Δ

(v) $PhC(S)NHNH_2$ / Piperidine / Ethanol, 50°C, US

(vi) $CH_3SC(S)NHNH_2$ / Piperidine / Ethanol, 50°C, US

(vii) $NH_2C(S)NHNH_2$ / Piperidine / Ethanol, 60°C, US

(viii) $CH_2(CN)COOEt$ / β-Alanine / AcOH / Benzene, Δ

(ix) NH_2CSNH_2 / Piperidine / Ethanol, Δ

Scheme I

triethylphosphonoacetate in the presence of $KOBu^t$ in dry DMSO under ultrasound conditions resulted in spiro cyclopropane derivative, ethyl 4,6-dimethyl-5,7-diphenyl-6-azaspiro[2.5]octane-1-carboxylate **3** with retention of configuration as per Denny's mechanism[7] (**Table I**). The ^{1}H NMR spectrum of **3** displayed two double doublets at δ 1.79 and 1.85 (C_2-H), a double doublet at δ 2.09 (C_8-H_{eq}), a multiplet around δ 2.36-2.49 (C_8-H_{ax} and C_4-H), a double doublet at δ 2.63 (C_1-H), a doublet at δ 3.30 (C_5-H) and a double doublet at δ 3.49 (C_7-H).

On the other hand, treatment of **1** with N-methyl-hydrazine produced *N*-methylhydrazone. Cyclization of the latter with thioglycolic acid gave 6,8-dimethyl-4-methyl-amino-7,9-diphenyl-1-thia-4,8-diazaspiro-[4.5]decan-3-one **4**, a novel spiro heterocyclic compound. The ^{1}H NMR spectrum displayed signals for different protons as a multiplet in the region δ 2.45-2.62 (C_6-H and C_{10}-H), a singlet at δ 3.28 (C_2-H), a doublet at δ 3.36 (C_7-H), a double doublet at δ 3.50 (C_9-H) and a singlet at δ 5.83 (NH).

Generally, the reaction of substituted hydrazines with aldehydes and ketones produces corresponding hydrazones. In fact, spiro thiadiazoline derivatives were prepared by cyclization of thiosemicarbazones of piperidinone derivatives using acetic anhydride[8].

Table I — Physical data of compounds **2-8**

Compd	m.p. (°C)	Yield (%)	Mol. formula (Mol. wt.)	Found % (Calcd) C	H	N
2a	106-08	58	$C_{20}H_{23}NO$ (293.40)	81.67 (81.87	7.81 7.90	4.83 4.77)
2b	120-22	15	-	-	-	-
3	92-93	67	$C_{24}H_{29}NO_2$ (363.49)	79.53 (79.30	8.12 8.04	3.78 3.85)
4	154-56	54	$C_{22}H_{27}N_3OS$ (381.54)	69.45 (69.26	7.01 7.13	11.18 11.01)
5	122-23	82	$C_{26}H_{27}N_3S$ (413.58)	75.26 (75.51	6.68 6.58	10.30 10.16)
6	168-70	73	$C_{21}H_{25}N_3S_2$ (383.58)	65.88 (65.76	6.49 6.57	10.82 10.95)
7	147-49	61	$C_{20}H_{24}N_4S$ (352.50)	68.32 (68.15	6.77 6.86	16.04 15.89)
8	186-88	45	$C_{25}H_{30}N_4O_2S$ (450.60)	66.50 (66.64	6.82 6.71	12.58 12.43)

Contrary to this, it was reported that the treatment of thioaroylhydrazine with an ethanolic solution of aldehyde or ketone in the absence of acidic catalyst gave cyclized product, 1,3,4-thiadiazoline directly[9]. Similarly, when the reaction of **1** was carried out with substituted hydrazines *viz*., thiobenzoylhydrazide, methylhydrazine carbodithioate and thiosemicarbazide in the presence of piperidine in ethanol resulted in 6,8-dimethyl-3,7,9-triphenyl-4-thia-1,2,8-triazaspiro[4.5]dec-2-ene **5**, 6,8-dimethyl-3-methyl-sulfanyl-7,9-diphenyl-4-thia-1,2,8-triazaspiro[4.5]dec-2-ene **6** and 3-amino-6,8-dimethyl-7,9-diphenyl-4-thia-1,2,8-triazaspiro[4.5]dec-2-ene **7**, respectively. The ^{1}H NMR spectrum of **5** displayed a double doublet at δ 2.46 (C_{10}-H_{eq}), a multiplet around δ 2.55-2.68 (C_6-H), a triplet at δ 2.85 (C_{10}-H_{ax}), a doublet at δ 3.30 (C_7-H), a double doublet at δ 3.57 (C_9-H) and a broad singlet at δ 9.03 (NH). The compounds **6** and **7** also exhibited signals almost in the same region as in the case of **5**. Apart from this, **6** showed a singlet at δ 2.59 for S-CH_3 and **7a** broad singlet at δ 5.69 for NH_2 at C-3.

Besides, the reaction of **1** with ethyl cyanoacetate gave an unsaturated cyano derivative, which on cyclocondensation with thiourea produced ethyl 2,4-diamino-7,9-dimethyl-8,10-diphenyl-1-thia-3,9-diaza-spiro[5.5]undeca-2,4-dien-5-carboxylate **8** (**Scheme I** and **Table I**). The ^{1}H NMR spectrum showed signals for different protons as a double doublet at δ 2.28 (C_{11}-H_{eq}), a multiplet at δ 2.36-2.48 (m, C_7-H and C_{11}-H_{ax}), a doublet at δ 3.30 (C_8-H) and a double doublet at δ 3.56 (C_{10}-H).

Thus, it is significant that 4-piperidone is utilized as a potential synthon for different heterocycles using modern synthetic tools such as ultrasonication and modified conventional routes. The structures of all the compounds were further confirmed from their ^{13}C NMR spectra.

Experimental Section

Melting points are uncorrected and were determined with Veego-PMP/DM apparatus. IR spectra were recorded on Perkin-Elmer FT-IR 1600 series spectrometer in KBr pellets. The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$/DMSO-d_6 on Brucker DPX-300 spectrometer operating at 300 MHz and 75.5 MHz, respectively. All chemical shifts were reported in δ (ppm) using TMS as an internal standard. The microanalyses were performed on Perkin-Elmer 240C elemental analyzer. All the solvents and reagents were obtained from commercial sources and purified before use as necessary. Ultrasonication was carried out by using Bandelin Sonorex Digitec RK 100H high-power ultrasonic-bath type sonicator. The compound **1** was prepared as per the procedure reported earlier[10].

General procedure for the synthesis of 4,6-dimethyl-5,7-diphenyl-1-oxa-6-azaspiro[2.5]octane 2. To a mixture of **1** (0.01 mole), TMSOI (0.013 mole) and dry DMSO (30 mL), KOBu^t (1.0 g) in dry DMSO (10 mL) was added dropwise for a period of 30 min while stirring. Then, the solution was sonicated in ultrasound-bath at RT for 2 hr. It was diluted with water and the agitation continued until a solid was separated out. It was filtered, dried and purified by recrystallization from alcohol. TLC showed two distinct spots indicating the formation of isomeric products **2a** and **2b**, which were separated by column chromatography (silica gel, 60-120 mesh, ethyl acetate:hexane, 1:3).

Compound **2a**: IR (KBr): 3025 (CH_2-O), 2768 (NCH_3), 1245 and 830 cm^{-1} (C-O-C); ^{1}H NMR: δ 0.62 (d, 3H, CH_3 at C-4), 1.97 (s, 3H, NCH_3), 2.13 (dd, 1H, C_8-H_{eq}, J = 14.0 and 3.4 Hz), 2.41-2.56 (m, 2H, C_4-H and C_8-H_{ax}), 2.68 and 2.89 (2d, 2H, C_2-H, J = 4.8 Hz), 3.27 (d, 1H, C_5-H_{ax}, J = 9.8 Hz), 3.52 (dd, 1H, C_7-H_{ax}, J = 14.2 and 3.6 Hz), 6.93-7.34 (m, 10H, Ar-H); ^{13}CNMR: δ 13.64 (CH_3 at C-4), 34.61 (C-8), 38.49 (C-4), 40.25 (NCH_3), 49.76 (C-2), 58.23 (C-3) 66.48 (C-7), 74.52 (C-5).

Compound **2b**: ^{1}H NMR: δ 1.13 (d, 3H, CH_3, J = 6.7 Hz), 2.10 (dd, 1H, C_8-H_{eq}, J = 13.6 and 3.4 Hz),

2.38-2.54 (m, 2H, C_4-H and C_8-H_{ax}), 2.65 and 2.91 (2d, 2H, C_2-H, *J* = 4.7 Hz), 3.25 (d, 1H, C_5-H_{ax}, *J* = 9.4 Hz), 3.54 (dd, 1H, C_7-H_{ax}, *J* = 13.8 and 3.5 Hz), 6.95-7.38 (m, 10H, Ar-H).

General procedure for the synthesis of ethyl 4,6-dimethyl-5,7-diphenyl-6-aza-spiro[2.5]octane-1-carboxylate 3. To a well stirred mixture of dry DMSO (20 mL) and $KOBu^t$ (1.0 g), triethylphosphonoacetate (0.0055 mole) was added dropwise till the evolution of gas ceased. Then, compound **2a** (0.005 mole) was added in portions over a period of 20 min and the mixture was sonicated at 65-70°C for 6 hr. The solution was then cooled and poured onto crushed ice. The solid separated was filtered and purified by recrystallization from alcohol.

Compound **3**: IR (KBr): 2760 (NCH_3), 1726 (Ester CO), 1190 cm^{-1} (C-O-C); ^{1}H NMR: δ 0.96-1.13 (m, 6H, CH_3 at C-4 and OCH_2CH_3), 1.79 (dd, 1H, C_2-H, *J* = 11.6 and 3.3 Hz), 1.85 (dd, 1H, C_2-H, *J* = 11.4 and 3.2 Hz), 1.92 (s, 3H, NCH_3), 2.09 (dd, 1H, C_8-H_{eq}, *J* = 14.2 and 3.5), 2.36-2.49 (m, 2H, C_8-H_{ax} and C_4-H), 2.63 (dd, 1H, C_1-H, *J* = 13.6 and 3.2 Hz), 3.30 (d, 1H, C_5-H, *J* = 10.0 Hz), 3.49 (dd, 1H, C_7-H, *J* = 14.4 and 3.6 Hz), 3.98 (q, 2H, OCH_2CH_3), 6.88-7.10 (m, 10H, Ar-H); ^{13}C NMR: δ 10.23 (CH_3 at C-4), 13.71 (OCH_2CH_3), 22.58 (C-2), 24.23 (C-3), 34.19 (C-8), 37.60 (C-4), 41.07 (NCH_3), 58.23 (OCH_2CH_3), 65.16 (C-7), 75.02 (C-5).

General procedure for the synthesis of 6,8-dimethyl-4-methylamino-7,9diphenyl-1-thia-4,8-diazaspiro[4.5]decan-3-one 4. To a solution of **1** (0.01 mole) in absolute alcohol (25 mL), methylhydrazine (0.015 mole) and a few drops of acetic acid were added. The contents were refluxed for 4 hr, cooled and diluted with water. The separated solid was filtered, dried and purified by recrystallization from aq. methanol. Yield 87%; m.p. 153-154°C. IR (KBr): 3286 (NH), 1632 cm^{-1} (C=N).

A mixture of above hydrazone (0.005 mole), thioglycolic acid (0.007 mole) and catalytic amount of Et_3N in DMF (25 mL) was refluxed for 10 hr. Then, the contents were poured into crushed ice and neutralized with $NaHCO_3$ solution. The solid was collected by filtration, dried and purified by recrystallization from alcohol.

Compound **4**: IR (KBr): 3326 (NH), 2765 (NCH_3), 1693 (C=O), 682 cm^{-1} (C-S-C); ^{1}H NMR: δ 1.06 (d, 3H, CH_3 at C-6), 2.13 (s, 3H, NCH_3), 2.36 (d, 3H, $NHCH_3$), 2.45-2.62 (m, 3H, C_6-H and C_{10}-H), 3.28 (s, 2H, C_2-H), 3.36 (d, 1H, C_7-H, *J* = 9.7 Hz), 3.50 (dd, 1H, C_9-H, *J* = 13.8 and 3.8 Hz), 5.83 (s, 1H, NH), 6.81-7.17 (m, 10H, Ar-H); ^{13}C NMR: δ 12.33 (CH_3 at C-4), 32.71 (C-10), 34.04 (C-6), 38.49 ($NHCH_3$), 41.22 (NCH_3), 44.60 (C-2), 65.32 (C-7), 74.07 (C-7), 80.23 (C-5), 171.25 (C-3).

General procedure for the synthesis of 6,8-dimethyl-3,7,9-triphenyl-4-thia1,2,8-triazaspiro[4.5]-dec-2-ene 5/6,8-dimethyl-3-methylsulfanyl-7,9-diphenyl-4-thia1,2,8triazaspiro[4.5]dec-2-ene 6/3-amino-6,8-dimethyl-7,9-diphenyl-4-thia1,2,8 triazaspiro[4.5]dec-2-ene 7. To the compound **1** (0.005 mole) in ethanol (20 mL), piperidine (5 drops) and thiobenzoyl-hydrazine/methylhydrazine carbodithioate/thiosemicarbazide (0.007 mole) was added and sonicated at 50-60°C for 4-5 hr. The contents were concentrated and cooled in an ice-bath. The solid separated was filtered, washed with aq. ethanol and purified by recrystallization from benzene-ethanol mixture.

Compound **5**: IR (KBr): 3284 (NH), 2761 (NCH_3), 1624 (C=N), 653 cm^{-1} (C-S); ^{1}H NMR: δ 0.93 (d, 3H, CH_3 at C-6), 2.07 (s, 3H, NCH_3), 2.46 (dd, 1H, C_{10}-H_{eq}, *J* = 13.8 and 3.7 Hz), 2.55-2.68 (m, 1H, C_6-H), 2.85 (t, 1H, C_{10}-H_{ax}), 3.30 (d, 1H, C_7-H, *J* = 10.2 Hz), 3.57 (dd, 1H, C_9-H, *J* = 14.0 and 3.6 Hz), 6.76-7.10 (m, 15H, Ar-H), 9.03 (s, 1H, NH); ^{13}C NMR: δ 12.93 (CH_3 at C-6), 39.86 (NCH_3), 43.71 (C-10), 45.87 (C-6), 66.54 (C-7), 75.85 (C-9), 83.32 (C-5), 153.86 (C-3).

Compound **6**: IR (KBr): 3262 (NH), 2753 (NCH_3), 1615 (C=N), 660 cm^{-1} (C-S); ^{1}H NMR: δ 0.88 (d, 3H, CH_3 at C-6), 1.72 (s, 3H, NCH_3), 2.41 (dd, 1H, C_{10}-H_{eq}, *J* = 14.4 and 4.0 Hz), 2.59 (s, 3H, SCH_3), 2.71-2.75 (m, 2H, C_6-H and C_{10}-H_{ax}), 2.93 (d, 1H, C_7-H, *J* = 9.7 Hz), 3.23 (dd, 1H, C_9-H, *J* = 13.7 and 3.8 Hz), 6.90-7.62 (m, 10H, Ar-H), 10.05 (s, 1H, NH); ^{13}C NMR: δ 13.70 (CH_3 at C-6), 19.06 (SCH_3), 39.35 (NCH_3), 43.92 (C-10), 45.71 (C-6), 67.28 (C-7), 75.22 (C-9), 85.60 (C-5), 155.07 (C-3).

Compound **7**: IR (KBr): 3240-3310 (NH and NH_2), 2770 (NCH_3), 1628 (C=N), 640 cm^{-1} (C-S); ^{1}H NMR: δ 1.05 (d, 3H, CH_3 at C-6), 2.19 (s, 3H, NCH_3), 2.38 (dd, 1H, C_{10}-H_{eq}, *J* = 14.2 and 3.9 Hz), 2.50-2.61 (m, 1H, C_6-H), 2.79 (t, 1H, C_{10}-H_{ax}), 3.39 (d, 1H, C_7-H, *J* = 10.0 Hz), 3.50 (dd, 1H, C_9-H, *J* = 14.2 and 3.8 Hz), 5.69 (bs, 2H, NH_2), 6.80-7.46 (m, 10H, Ar-H). ^{13}C NMR: δ 12.63 (CH_3 at C-6), 40.08 (NCH_3), 44.13 (C-10), 46.52 (C-6), 65.80 (C-7), 76.03 (C-9), 84.22 (C-5), 158.45 (C-3).

General procedure for the synthesis of ethyl 2,4-diamino-7,9-dimethyl-8,10-diphenyl-1-thia-3,9-diazaspiro[5.5]un-deca-2,4-dien-5-carboxylate 8. A

mixture of **1** (0.01 mole), ethyl cyanoacetate (0.012 mole), β-alanine (catalytic amount), acetic acid (few drops) and dry benzene (50 mL) was refluxed using Dean-Stark apparatus until the separation of water ceased. The contents were cooled, diluted with benzene and washed with saturated $NaHCO_3$ solution and water. The organic layer was dried over anhyd. Na_2SO_4. Evaporation of solvent gave a semisolid product, which was purified by recrystallization from ethanol. Yield 68%, m.p. 108-110°C. IR (KBr): 2216 (C≡N), 1720 (COOEt), 1625 cm^{-1}(C=C).

A solution of the above unsaturated cyano derivative (0.005 mole), thiourea (0.008 mole) and piperidine (0.5 mL) in ethanol (25 mL) was refluxed for 5 hr. The contents were cooled and poured into crushed ice. The separated solid was filtered and purified by column chromatography (silica gel, 60-120 mesh, ethyl acetate:hexane, 1:2).

Compound **8**: IR (KBr): 3240-3320 (NH_2), 2772 (NCH_3), 1728 (Ester CO), 1626 (C=N), 1582 (C=C), 675 cm^{-1} (C-S); ^{1}H NMR: δ 1.13-1.26 (m, 6H, CH_3 at C-7 and OCH_2CH_3), 2.20 (s, 3H, NCH_3), 2.28 (dd, 1H, C_{11}-H_{eq}, *J* = 13.8 and 4.0 Hz), 2.36-2.48 (m, 2H, C_7-H and C_{11}-H_{ax}), 3.30 (d, 1H, C_8-H, *J* = 9.8 Hz), 3.56 (dd, 1H, C_{10}-H, *J* = 13.8 and 3.6 Hz), 4.07 (q, 2H, OCH_2CH_3), 6.63-7.15 (m, 14H, Ar-H and $2NH_2$ at C-2 and C-4). ^{13}C NMR: δ 12.36 (CH_3 at C-7), 13.61 (OCH_2CH_3), 36.55 (C-11), 38.62 (C-7), 40.1 (NCH_3), 56.27 (C-6), 59.03 (OCH_2CH_3), 67.18 (C-8), 74.82 (C-10), 110.66 (C-5), 153.28 (C-4), 164.12 (C-2), 168.75 (ester CO).

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