Regioselective Acylations of Ketones to 1,3-Diketones via Metalated Dimethylhydrazones[1]

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Acyclic and cyclic unsymmetrical ketones **1** are regioselectively acylated via their corresponding metalated dimethylhydrazones **3** by using acid chlorides or anhydrides, arylnitriles, ethyl formate, carbon disulfide/methyl iodide, alkyl chloroformates, dialkyl carbonates, phenyl isocyanate, or phenyl isothiocyanate as acylating agents. Subsequent acidic hydrolysis leads to the 1,3-diketones **6** in acceptable to excellent overall yields. The tautomeric structure of the product hydrazones **4**, **5**, **7**, and **8** is determined. Cyanation of **3** with cyanogen bromide affords the α-cyano dimethylhydrazones **9**.

The chemistry of 1,3-diketones and related derivatives has attracted much interest due to their practical applications in such diverse areas as analysis of lunar samples, estimation of vitamin B_{12}, NMR shift reagents, laser chelates, and in general, as basic key structures in chemistry[2]. Among the various methods for their synthesis, the acylation of ketones represents the most straightforward entry to 1,3-diketones[3,4], and many reactions of metal enolates with acylating agents, such as acid chlorides[5–15], acid anhydrides[16], esters[17,18], acyl cyanides[19], acylimidazoles[20–24], mixed anhydrides[25,26], acylsilanes[27], dialkyl acylphosphonates[28], carbon disulfide/alkyl halides[29], *O*-alkyl *S*-ethyl dithiocarbonates[30], dialkyl carbonates[31], and *N*-methoxy-*N*-methylamides[32] have been described. The oxidation of β-hydroxy ketones to form 1,3-diketones has also been reported[33].

However, it is a well-known fact that 1:1 acylations of metal enolates are associated with various problems, such as *O*- and diacylations, proton exchange between the enolate and the acylation product and thus low yields, as well as the formation of regioisomers[34]. To circumvent these problems, several alternatives have been developed as, for instance, the strict control of reaction conditions[35] or the use of indirect methods by employing enamines[36–39], enaminosilanes[40], silyl enol ethers[41–44], boron enol ethers[45], metalated imines[46], and metalated dimethylhydrazones[1,29,30,32] as enolate equivalents in acylation reactions.

We now wish to report the experimental details of an efficient and regioselective 1:1 acylation of ketones to 1,3-diketones with acid chlorides, acid anhydrides, esters, arylnitriles and dialkyl carbonates based on the dimethylhydrazone method[47].

Results and Discussion

Metalated dimethylhydrazones (DMHs) have proven to be versatile enolate equivalents in a variety of electrophilic substitutions α to the carbonyl group of aldehydes and ketones, and problems of classical carbonyl chemistry mentioned above could be solved efficiently[47]. This turned out to be true also in acylation reactions by employing a great variety of acylating electrophiles. As depicted in Scheme 1, cyclic and acyclic, mainly unsymmetrical, ketones **1** were converted into their corresponding dimethylhydrazones **2**, which in turn were metalated with *n*-butyllithium in tetrahydrofuran (THF) at −78 °C (methyl ketone DMHs) or lithium diisopropylamide (LDA) at 0 °C to yield the lithiated species **3**. The THF suspension of the azaenolates **3** thus obtained was then added to a solution of the acylation reagent (acid chloride, anhydride, ester, or arylnitrile) in THF at −78 °C, which after quenching and workup resulted in the formation of the acylated hydrazones **4** and **5**, respectively. Finally, **4** and **5** were dissolved in methanol and hydrolyzed with 2 N HCl under heating to the desired 1,3-diketones **6**, which are thus available in a regioselective way and with acceptable to excellent overall yields (see Experimental).

When the lithiated DMHs **3** were trapped with acid chlorides, ethyl formate, or acid anhydrides, the hydrazones **4**[48] were obtained, which according to the spectroscopic data (IR, ^{1}H and ^{13}C NMR) in the cases of R^2 = H (**4a–f,m**) entirely exist as the keto-enehydrazine tautomers **4A**. The only exception was **4d**, where the ^{13}C-NMR data indicated a small amount of another isomer, probably the enol-hydrazone tautomer **4C**. The keto-hydrazone tautomer **4B** could not be detected in any case. Structure **4A** is also present in the acyclic, substituted (R^2 = Ph) compound **4g**, obviously due to a favourable π-configuration of the double bond with the phenyl ring R^2. In all other cases, where cyclic ketones **1** were used as starting material ($R^2 \neq$ H; **4h–l**), the keto-hydrazone structure **4B** predominated over **4A**. Additional isomers detected in the case of **4h–j** are assigned to (*E*)/(*Z*) or *cis*/*trans* isomers of the tautomeric structure **4B**. The hydrazone derivative **4m** is the DMH precursor of a major component of the defense secretion of the termite *Rhinotermes hispidus* Emerson[49].

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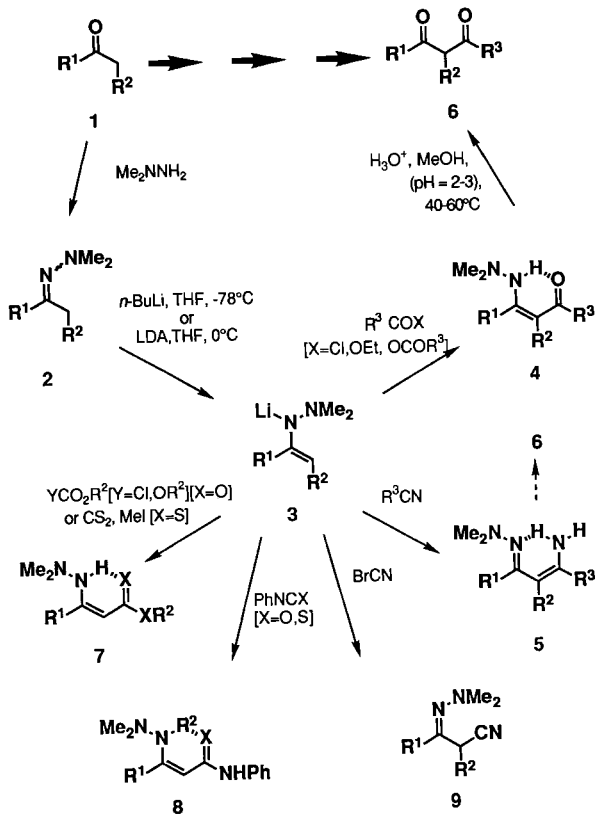
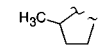
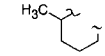
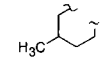
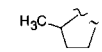
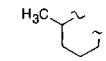
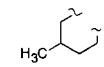
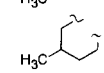
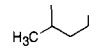
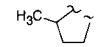
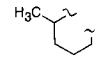
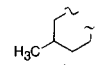
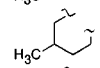
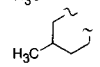
Scheme 1



2, 3	R^1	R^2
a	Me	H
b	Et	H
c	*n*Pr	H
d	*i*Pr	H
e		
f	$[CH_2]_4$	
g		
h		
i	Me	Ph
j	*n*-$C_{11}H_{23}$	H

4	R^1	R^2	R^3
a	*n*Pr	H	Me
b	*n*Pr	H	Et
c	*n*Pr	H	*i*Pr
d	*i*Pr	H	*n*-$C_{11}H_{23}$
e	Me	H	Ph
f	*n*Pr	H	Ph
g	Me	Ph	Ph
h			*t*Bu
i	$[CH_2]_4$		*t*Bu
j			*i*Pr
k			*i*Pr
l			*t*Bu
m	*n*-$C_{11}H_{23}$	H	H

	R^1	R^2	R^3
5a	*n*Pr	H	Ph
b	*i*Pr	H	4-BrC_6H_4
c	Et	H	2-Naph
d			4-BrC_6H_4
6a	*n*Pr	H	Et
b	*n*Pr	H	*i*Pr
c	*i*Pr	H	*n*-$C_{11}H_{23}$
d	*n*Pr	H	Ph
e	Me	Ph	Ph
f	*i*Pr	H	4-BrC_6H_5
g	Et	H	2-Naph
h			*t*Bu
i	$[CH_2]_4$		*t*Bu
j			*i*Pr
k			*i*Pr
l			*t*Bu
m			4-BrC_6H_4

	R^1	R^2	X
7a	*n*Pr	Me	O
b	*n*Pr	Et	O
c	*n*Pr	Me	S
8a	*n*Pr	H	S
b	Me	H	O
c	*n*Pr	H	O

9	R^1	R^2
a	$[CH_2]_4$	
b	$[CH_2]_3$	

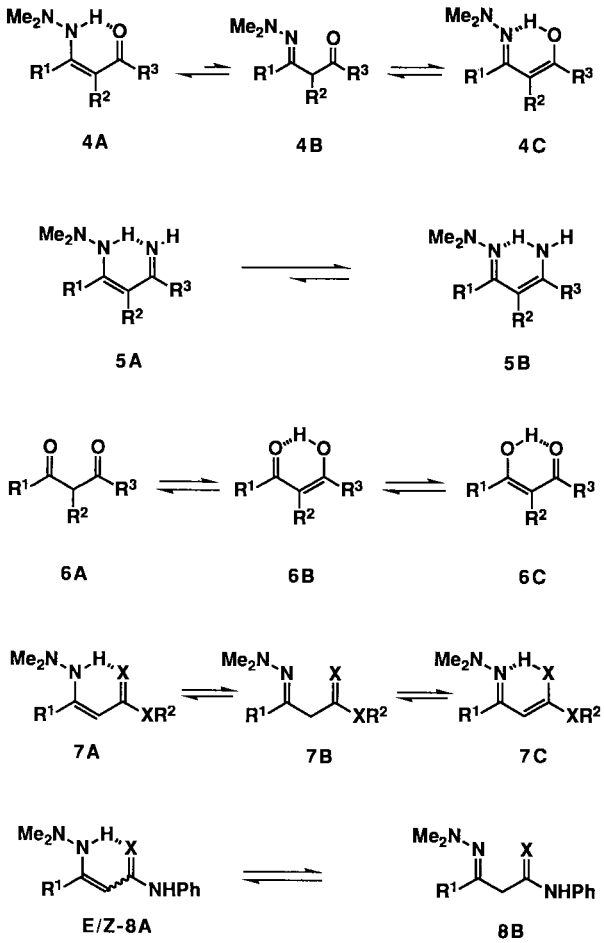
When aromatic nitriles were used as acylating agents, the hydrazones **5** are formed, which in the case of the acyclic compounds **5a–c** entirely exist in the enamino-hydrazone form **5B**. This is evident from the appearance of an NH_2 absorption band in the region of $\tilde{\nu} = 3110-3460\ cm^{-1}$ (IR) and a broad NH_2 singlet in the range of $\delta = 6.2-6.85$ (^1H NMR). For the cyclic compound **5d**, however, a mixture of **5B** (83%) and the imino-enehydrazine tautomer **5A** (17%) was detected in $CHCl_3$ by ^1H-NMR spectroscopy (imino H: $\delta = 12.18-14.44$).

The 1,3-diketones **6** were purified by distillation or recrystallization, in some cases by using their corresponding copper chelates. Depending on the groups R^1-R^3 and the solvents used, the diketo and keto-enol tautomers **6A,B** and/or **C** could be detected by IR and NMR spectroscopy. In the case of the acyclic 1,3-diketones **6a–g** (R^2 = H) the keto-enol form **6B** predominates in $CDCl_3$ solution (^1H NMR: olefinic H: $\delta = 5.42-6.18$) besides small amounts of **6A**, whereas in the less polar solvent CCl_4 only the keto-enol tautomer **6B** is detectable. This is especially the case for **6d–g**, which bear an aromatic substituent as R^3 leading to a more stable styryl conjugation, rather than an aroyl system, as would be the case in form **6C**[50]. In the cyclic diketones **6h–m** ($R^2 \neq$ H) the diketo tautomer **6A** predominates (^1H NMR: methine H: $\delta = 3.47-4.20$) in some examples as a mixture of *cis/trans* isomers, beside the keto-enol form **6C** having an endocyclic double bond. The direction of enolization in **6m** is again towards the aryl moiety.

In order to test the scope and limitations of the new acylation procedure, a variety of other acylation reactions were performed by trapping **3** with electrophiles, such as methyl chloroformate, dimethyl carbonate, carbon disulfide/methyl iodide, phenyl isocyanate and phenyl isothiocyanate. The DMH acylations with methyl chloroformate and dialkyl carbonates gave the hydrazone esters **7a** and **b** in moderate yields, respectively. The spectroscopic data indicate the presence of the keto-enehydrazone form **7A** and small amounts of the keto-hydrazone form **7B**. Trapping of the lithiated DMHs **3** with CS_2, followed by addition of methyl iodide afforded **7c** in 89% yield. In contrast to **7a** and **b** (X = O), the dithioester **7c** (X = S) exists as the hydrazono-enethiol tautomer **7C**, as was evident from the spectroscopic data [IR: $\tilde{\nu} = 2200\ cm^{-1}$ (hydrogen-bridged SH); ^1H NMR: olefinic H: $\delta = 6.03$, SH singlet: $\delta = 14.16$).

The acylation of **3** with phenyl isothiocyanate or phenyl isocyanate afforded the hydrazone (thio)amides **8a–c** in good to excellent yields, which mainly exist as enehydrazino-(thio)amide tautomers **8A**. Whereas in **8a** (X = S) only one isomer was detectable, the NMR and IR data of **8b** and **c** (X = O) indicated the presence of three isomers, which were

Scheme 2



assigned to (*E*)/(*Z*)-**8A** and **8B**, respectively. In the latter two cases a very small amount (< 1%) of a diacylated product (R^2 = CONHPh) could also be detected by high-resolution MS (see Experimental).

Finally, it could be shown that trapping of metalated DMHs **3** with cyanogen bromide leads to α-cyano dimethylhydrazones **9** (IR: C≡N absorption: $\tilde{\nu}$ = 2250–2260 cm^{-1}) and thus opens a regioselective entry to α-cyano ketones.

In conclusion, we have demonstrated that regioselective 1:1 acylations at the less substituted α-carbon atom of unsymmetrical acyclic and cyclic ketones as well as cyanations are possible in a general way via the corresponding DMH derivatives and by employing the whole palette of different acylating agents.

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Experimental

Melting points (uncorrected): Büchi SMP 20. – IR: Perkin-Elmer 225, 157G, or Beckman Acculab 4. – NMR ($CDCl_3$ or CCl_4, tetramethylsilane as internal standard): Varian EM 360, Bruker WH-90, Jeol Minimar 100, or Varian VXR 300. – MS: AEI MS-9, MS-30, Varian MAT 212, or GC/MS system MAT 111. – Elemental analyses: Heraeus CHN-O-Rapid.

Synthesis of Ketone Dimethylhydrazones: 2-Propanone dimethylhydrazone (**2a**)[47], 2-butanone dimethylhydrazone (**2b**)[51], 2-pentanone dimethylhydrazone (**2c**)[47,52], 3-methyl-2-butanone dimethylhydrazone (**2d**)[47], cyclohexanone dimethylhydrazone (**2f**)[51,53], 2-methylcyclohexanone dimethylhydrazone (**2g**)[47], and 3-methylcyclohexanone dimethylhydrazone (**2h**)[47], and 1-phenyl-2-propanone dimethylhydrazone[47] (**2i**) were prepared by literature procedures.

2-Methylcyclopentanone Dimethylhydrazone (**2e**): 3.15 g (25 mmol) of cyclopentanone dimethylhydrazone was metalated with lithium diisopropylamide (25 mmol) in 50 ml of THF at 0°C, and methylated with 1.55 ml (25 mmol) of methyl iodide at −78°C. After aqueous workup, 2.78 g (79%) of **2e** as a light yellow liquid, b.p. 61°C/20 Torr or 80°C/62 Torr, was obtained. – IR (neat): $\tilde{\nu}$ = 2960 cm^{-1}, 2860, 2820, 2750, 1660 (C=N), 1470, 1455, 1425, 1375, 1215, 1180, 1155, 1090, 1020, 975, 935, 845. – ^1H NMR (CCl_4): δ = 1.10 (d, 3H, 2-CH_3), 1.44–2.08 (m, 4H, 3-, 4-H_2), 2.10–2.48 (m, 3H, 2-H, 5-H_2), 2.39 [s, 6H, $N(CH_3)_2$]. – MS (80 eV): *m/z* (%) = 140 (20) [M^+].

$C_8H_{16}N_2$ (140.2) Calcd. C 68.51 H 11.50 N 19.98
Found C 68.60 H 11.52 N 19.98

2-Tridecanone Dimethylhydrazone (**2j**): 9.92 g (50.0 mmol) of 2-tridecanone was mixed with 7.60 ml (100 mmol) of *N,N*-dimethylhydrazine and 10.0 g (62.2 mmol) of BaO. The resultant mixture was heated at 85–90°C (bath temp.) for 4 h, and excess of *N,N*-dimethylhydrazine was distilled off. The reaction mixture was then filtered to yield **2j** as a colorless liquid, 12.0 g (99%), b.p. 120 to 122°C/0.8 Torr. – IR (neat): $\tilde{\nu}$ = 2980 cm^{-1}, 2960, 2910, 2840, 2805, 2762, 1638 (C=N), 1465, 1355, 1300, 1250, 1220, 1198, 1150, 1115, 1090, 1020, 965, 810, 720. – ^1H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 6.38, 3H, CH_3CH_2), 1.26 (m, 16H, $[CH_2]_8$), 1.49 (m, 2H, $CH_3CH_2CH_2$), 1.94 (s, 3H, CH_3C=N), 2.16 (t, *J* = 8.06 Hz, 2H, CH_2C=N), 2.42 [s, 6H, $N(CH_3)_2$]. – ^{13}C NMR ($CDCl_3$): δ = 14.2 (C-13); 16.4 (C-1); 22.6, 22.7, 26.6, 27.1, 29.3, 29.4, 29.5, 29.6, 29.7, 29.9, 31.5, 32.0 [C-3–C-12, (*E*)/(*Z*)]; 47.0, 47.5 [$N(CH_3)_2$, (*E*)/(*Z*)]; 168.0, 169.6 [C-2, (*E*)/(*Z*)]. – MS (70 eV): *m/z* (%) = 241 (1) [M^+ + 1], 240 (6) [M^+], 196 (5) [M^+ − $N(CH_3)_2$], 113 (6), 101 (3), 100 (45), 99 (2), 98 (2), 96 (2), 95 (1), 85 (3), 84 (3), 83 (3), 82 (3), 81 (2), 79 (2), 72 (2), 71 (4), 70 (14), 69 (5), 68 (2), 67 (3), 61 (3), 60 (100) [$C_2H_8N_2^+$], 59 (9), 58 (68), 57 (11), 56 (12), 55 (11), 54 (2), 53 (2), 45 (23), 44 (71) [$N(CH_3)_2^+$], 43 (24), 42 (25), 41 (25), 40 (2), 39 (7).

$C_{15}H_{32}N_2$ (240.4) Calcd. C 74.93 H 13.41 N 11.65
Found C 74.90 H 13.58 N 11.84

Synthesis of the Acylated Hydrazones **4** *and* **5** (General Procedure I): The methyl ketone dimethylhydrazones (DMHs) **2** (10 mmol) were metalated in absol. THF under argon at −78°C with *n*-butyllithium (7.5 ml, 1.5 N solution in *n*-hexane, 11.5 mmol) as described previously[47]. The other ketone DMHs **2** were metalated with lithium diisopropylamide (11 mmol) in absol. THF at 0°C as reported earlier[47]. The required time for the completion of metalation varied from 15 min to 1 h depending upon the nature of the ketone DMH. The suspension of the lithiated DMH in THF thus obtained was added to a solution of the acylating agent (acid chloride, acid anhydride, ester or nitrile; 10 mmol in 20 ml THF) at −78°C. The reaction mixture was stirred (12–15 h), and the tem-

perature was raised to 0°C. The resulting acylation product was quenched with acetic acid [0.75 ml (10 mmol)], and the organic phase was separated by addition of an appropriate amount of a saturated solution of NH_4Cl. The aqueous phase was extracted with CH_2Cl_2, the combined organic phases were washed with water, dried with anhydrous Na_2SO_4, and filtered. The CH_2Cl_2 was removed under reduced pressure to yield **4** or **5**, respectively. The compounds **4** and **5** were purified by distillation under reduced pressure or by recrystallization form a suitable solvent.

Hydrolysis of the Acylated Hydrazones **4** *and* **5** *to the 1,3-Diketones* **6** (General Procedure II): The hydrazones **4** and **5** (5−10 mmol) were dissolved in MeOH (20−25 ml). Hydrochloric acid (2 N, 15 ml) was added, and the resulting mixture was heated to reflux at 80−90°C (bath temperature) for 5 h, then cooled to room temperature, and extracted with CH_2Cl_2 (3 × 50 ml). The combined CH_2Cl_2 extracts were washed with water (3 × 20 ml) and dried with anhydrous Na_2SO_4. The CH_2Cl_2 was removed under reduced pressure to yield the diketones **6**. They were purified by distillation, recrystallization, or through their copper chelates. In the case of compounds **6c,f**, and **g** the pure 1,3-diketone was regenerated by treatment of the corresponding copper chelate with 5 N HCl, extraction with ether, followed by either distillation under reduced pressure or recrystallization from a suitable solvent.

Preparation of Copper Chelates of **6** (General Procedure III): To a solution of **6** (5−10 mmol) in MeOH (50 ml) was added a clear, hot solution of $Cu(OAc)_2$ in water [prepared by dissolving 2.0 g (11 mmol) of $Cu(OAc)_2$ in 50 ml of water, heating to boiling, and filtering]. The mixture was heated in a water bath at 80−90°C for 2 h, cooled, and filtered. The copper chelate thus obtained was washed with petroleum ether (boiling range 40−60°C) (3 × 50 ml) followed by recrystallization from MeOH or $CHCl_3$.

Synthesis of Acylated Hydrazones **7** *and* **8** (General Procedures IV and V). − *Method IV:* To a solution of acylating reagent (10 mmol) in THF (20 ml) cooled to −78°C was added the THF suspension of metalated methyl ketone DMH (11 mmol) in 20 ml of THF. The reaction mixture was stirred for ca. 12 h, and the temperature was raised to 0°C. The resultant mixture was neutralized with glacial acetic acid [0.65 ml (11 mmol)] or directly quenched with a saturated aqueous solution of NH_4Cl. The organic phase was extracted with CH_2Cl_2 (3 × 50 ml), and the combined extracts were washed with water and dried with anhydrous Na_2SO_4. The CH_2Cl_2 was removed under reduced pressure to yield **7** or **8**, which were further purified by distillation under reduced pressure or recrystallized from a suitable solvent.

Method V (Reversed Sequence): A solution of acylating reagent (10 mmol) in THF (20 ml), cooled to −78°C, was added to the suspension of metalated methyl ketone DMH (11 mmol) in 20 ml of THF at −78°C.

4-(N,N-Dimethylhydrazino)-3-hepten-2-one (**4a**): According to the general procedure I 0.79 g (10 mmol) of acetyl chloride was treated with metalated **3c**, prepared from 1.28 g (10 mmol) of **2c**, to yield 0.64 g (38%) of **4a**. Alternatively, **4a** was prepared by treatment of 1.02 g (10 mmol) of acetic anhydride with **3c** to yield 0.95 g (56%) as a yellow oil, b.p. 60°C (bath)/0.02 Torr. − IR (neat): $\tilde{\nu}$ = 2960 cm^{-1}, 2870, 2820, 2780, 1610 (C=O), 1575 (C−N), 1505, 1465, 1450, 1430, 1355, 1300, 1265, 1210, 1190, 1160, 1085, 1010, 980, 910, 740. − ^1H NMR (CCl_4): δ = 1.05 (t, 3H, CH_3), 1.67 (m, 2H, 6-H_2), 1.96 (s, 3H, CH_3CO), 2.14−2.47 (m, 2H, 5-H_2), 2.64 [s, 6H, $N(CH_3)_2$], 4.84 (s, 1H, 3-H), 11.36 (s, 1H, N−H···O, H/D exchange). − ^{13}C NMR ($CDCl_3$): δ = 14.0 (C-7), 22.0 (C-6), 28.7 (C-1), 33.7 (C-5), 48.7 [$N(CH_3)_2$], 92.8 (C-3), 166.8 (C-4), 194.9 (C-2). − MS (80 eV): *m/z* (%) = 170 (18) [M^+], 127 (17) [$M^+ - CH_3CO$], 126 (11) [$M^+ - N(CH_3)_2$], 112 (26), 99 (15), 84 (15), 71 (9), 70 (8), 60 (9), 59 (15), 58 (20), 57 (11), 56 (9), 45 (54), 44 (100) [$N(CH_3)_2^+$], 43 (71) [CH_3CO^+], 42 (99) [$CH_2=C=O^+$], 41 (50), 40 (11), 39 (16), 29 (15), 15 (16).

$C_9H_{18}N_2O$ (170.3) Calcd. C 63.48 H 10.65 N 16.46
Found C 63.36 H 10.52 N 16.30

5-(N,N-Dimethylhydrazino)-4-octen-3-one (**4b**): According to the general procedure I 0.93 g (10 mmol) of propanoyl chloride was treated with **3c**, prepared from 1.28 g (10 mmol) of **2c**, to yield 1.17 g (64%) of an orange-red oil, b.p. 60−70°C (bath)/0.015 Torr. − IR (neat): $\tilde{\nu}$ = 2960 cm^{-1}, 2930, 2870, 2820, 2775, 1605 (C=O), 1575 (C−N), 1505, 1455, 1430, 1345, 1285, 1250, 1230, 1210, 1150, 1085, 1035, 1010, 920, 750. − ^1H NMR (CCl_4): δ = 0.98, 1.03 (2 t, 6H, 2 CH_3, overlapped); 1.34−1.78 (m, 2H, 7-H_2); 1.94−2.40 (m, 4H, 2-, 6-H_2); 2.57 [s, 6H, $N(CH_3)_2$]; 4.75 (s, 1H, 4-H); 11.25 (s, N−H···O, H/D exchange). − ^{13}C NMR ($CDCl_3$): δ = 9.9 (C-1), 14.0 (C-8), 22.1 (C-7), 33.8 (C-6), 34.7 (C-2), 48.7 [$N(CH_3)_2$], 91.8 (C-4), 166.5 (C-5), 198.5 (C-3).

$C_{10}H_{20}N_2O$ (184.3) Calcd. C 65.17 H 10.19 N 15.19
Found C 65.05 H 10.80 N 14.90

5-(N,N-Dimethylhydrazino)-2-methyl-4-octen-3-one (**4c**): According to the general procedure I 1.07 g (10 mmol) of isobutyryl chloride was treated with **3c**, prepared from 1.28 g (10 mmol) of **2c**, to yield 1.06 g (81%) of a yellow oil, b.p. 70°C (bath)/0.02 Torr or 100°C/0.3 Torr. − IR (neat): $\tilde{\nu}$ = 2960 cm^{-1}, 2930, 2865, 2820, 2780, 1610 (C=O), 1570 (C−N), 1505, 1460, 1445, 1425, 1375, 1350, 1295, 1250, 1210, 1135, 1090, 1010, 920, 845, 770, 715. − ^1H NMR (CCl_4): δ = 0.84−1.20 (m, 9H, 3 CH_3), 1.34−1.80 (m, 2H, 7-H_2), 2.06−2.42 [m, 3H, 6-H_2, C*H*$(CH_3)_2$], 2.58 [s, 6H, $N(CH_3)_2$], 4.74 (s, 1H, 4-H), 11.30 (s, N−H···O). − ^{13}C NMR ($CDCl_3$): δ = 14.0 (C-8), 19.9 (C-1), 22.0 (C-7), 33.7 (C-6), 39.5 (C-2), 48.8 [$N(CH_3)_2$], 90.6 (C-4), 167.2 (C-5), 202.3 (C-3).

$C_{11}H_{22}N_2O$ (198.3) Calcd. C 66.61 H 11.18 N 14.12
Found C 66.83 H 11.39 N 13.96

3-(N,N-Dimethylhydrazino)-2-methyl-3-hexadecen-5-one (**4d**): According to the general procedure I 2.3 ml (10 mmol) of dodecanoyl chloride was treated with **3d**, prepared from 1.45 g (11.3 mmol) of **2d**, to yield 3.0 g (96%) of a viscous, yellow oil, b.p. 140−145°C/0.3 Torr. − IR (neat): $\tilde{\nu}$ = 3350−3200 cm^{-1} (br., NH, OH), 1615 (C=O), 1575 (C−N). − ^1H NMR ($CDCl_3$): δ = 1.01 [t, 3H, 16-H_3], 1.10−1.20 [d, 6H, $CH(CH_3)_2$], 1.25−2.00 [m, 18H, 7−15-H_2], 2.18−2.44 [t, 2H, 6-H_2], 2.80 [m, 1H, C*H*$(CH_3)_2$], 2.58 [s, 6H, $N(CH_3)_2$], 5.48 (s, 1H, 4-H), 11.90 (s, 1H, N−H···O). − ^{13}C NMR ($CDCl_3$): δ = 13.7, 14.1, 19.2, 21.6, 22.7, 23.1, 25.0, 25.1, 26.2, 28.1, 28.7, 29.2, 29.4, 29.6, 29.7, 30.8, 31.9, 32.0, 34.5 (C-6−16); 19.9 [$(CH_3)_2CH$]; 39.4 [$(CH_3)_2CH$]; 48.9, 48.8 [$N(CH_3)_2$, keto/enol form]; 90.4 (C-4, keto form); 88.3 (C-4, enol form); 167.9 (C-3); 193.0 (C-5, enol form); 202.4 (C-5, keto form). − MS (70 eV): *m/z* (%) = 311.3022 (6.47) [$M^+ + 1$], 310.2996 (28.55) [M^+], 43.0587 (100) [$C_3H_7^+$].

$C_{19}H_{38}N_2O$ (310.3) Calcd. C 73.49 H 12.33 N 9.02
Found C 73.62 H 12.60 N 9.25

3-(N,N-Dimethylhydrazino)-1-phenyl-2-buten-1-one (**4e**): According to the general procedure I 1.44 g (10 mmol) of benzoyl chloride was treated with **3a**, prepared from 1.00 g (10 mmol) of **2a**, to yield 1.60 g (78%) of **4e**. Alternatively, **4e** was prepared by treatment of 4.05 g (25 mmol) of benzoyl acetone with 2.40 g (40 mmol) of *N,N*-dimethylhydrazine in benzene (10 ml) to give 1.87 g (92%) of **4e** as a highly viscous, yellow, undistillable oil. − IR (neat): $\tilde{\nu}$ = 3060 cm^{-1}, 2980, 2950, 2860, 2820, 2775, 1595 (C=O), 1550, 1445,

1425, 1370, 1315, 1290, 1220, 1175, 1155, 1090, 1065, 1025, 920, 850. – ^{1}H NMR (CCl_4): δ = 2.08 (s, 3H, CH_3), 2.60 [s, 6H, $N(CH_3)_2$], 5.42 (s, 1H, 2-H), 7.08–7.58 (m, 3H, *m*-, *p*-H), 7.59–8.03 (m, 2H, *o*-H), 11.86 (s, 1H, N–H···O, H/D exchange). – ^{13}C NMR ($CDCl_3$): δ = 18.4 (C-4); 48.3 [$N(CH_3)_2$]; 90.1 (C-2); 126.9, 128.1, 130.4, 140.3 (aromatic C); 164.4 (C-3); 187.6 (C-1). – MS (80 eV): *m/z* (%) = 204 (39) [M^+], 161 (17) [$M^+ - CH_3CO$], 160 (71) [$M^+ - N(CH_3)_2$], 129 (12), 120 (7), 105 (71) [$C_6H_5CO^+$], 102 (23), 99 (76) [$M^+ - 105$], 91 (9), 84 (31) [$M^+ - 120$], 78 (12), 77 (67) [$C_6H_5^+$], 76 (12), 59 (19), 58 (14), 56 (88), 51 (28) [$C_4H_3^+$], 50 (12), 45 (37), 44 (100) [$N(CH_3)_2^+$], 43 (31) [CH_3CO^+], 42 (52), 41 (33), 39 (14).

$C_{12}H_{16}N_2O$ (204.3) Calcd. C 70.55 H 7.90 N 13.72
Found C 70.54 H 7.84 N 13.70

3-(N,N-Dimethylhydrazino)-1-phenyl-2-hexen-1-one (**4f**): According to the general procedure I 1.41 g (10 mmol) of benzoyl chloride was treated with **3c**, prepared from 1.28 g (10 mmol) of **2c**, to yield 1.79 g (77%) of **4f**. A 1:2-ratio experiment of benzoyl chloride and **2c** followed by quenching with acetic acid gave **4f** in <40% spectroscopic yield. Alternatively, **4f** was prepared by treatment of 1.31 g (10 mmol) of benzoyl cyanide with **3c** (10 mmol) to give 1.95 g (84%) of a highly viscous, yellow, undistillable oil. – IR (neat): $\tilde{\nu}$ = 3060 cm^{-1}, 2960, 2870, 2820, 2780, 1585 (C=O), 1550, 1460, 1450, 1340, 1320, 1300, 1290, 1270, 1160, 1095, 1065, 1020, 1010, 920, 740, 710, 690. – ^{1}H NMR (CCl_4): δ = 1.01 (t, 3H, CH_3), 1.24–1.95 (m, 2H, 5-H_2), 2.32–2.51 (m, 2H, 4-H_2), 2.58 [s, 6H, $N(CH_3)_2$], 5.48 (s, 1H, 2-H), 7.19–7.60 (m, 3H, *m*-, *p*-H), 7.71–7.95 (m, 2H, *o*-H), 11.85 (s, 1H, N–H···O). – ^{13}C NMR ($CDCl_3$): δ = 14.0 (C-6); 22.0 (C-5); 34.1 (C-4); 48.7 [$N(CH_3)_2$]; 89.4 (C-2); 127.0, 128.1, 130.4, 140.5 (aromatic C); 168.4 (C-3); 187.9 (C-1). – MS (80 eV): *m/z* (%) = 232 (17) [M^+], 189 (14) [$M^+ - C_3H_7$], 188 (34) [$M^+ - N(CH_3)_2$], 174 (14), 127 (14) [$M^+ - C_6H_5CO$], 125 (15), 105 (100) [$C_6H_5CO^+$], 102 (21), 77 (52) [$C_6H_5^+$], 51 (17), 45 (35), 44 (64) [$N(CH_3)_2^+$], 43 (32 [$C_3H_7^+$], 42 (63), 41 (34), 29 (15).

$C_{14}H_{20}N_2O$ (232.3) Calcd. C 72.37 H 8.68 N 12.06
Found C 72.41 H 8.79 N 11.93

3-(N,N-Dimethylhydrazino)-1,2-diphenyl-2-buten-1-one (**4g**): According to the general procedure I 1.41 g (10 mmol) of benzoyl chloride was treated with **3i**, prepared from 1.76 g (10 mmol) of **2i**, to afford 2.54 g (91%) of **4g** which crystallized as yellow needles, m.p. 107°C (*n*-pentane). – IR (KI): $\tilde{\nu}$ = 3080 cm^{-1}, 3050, 2955, 2860, 2820, 2780, 1570 (C=O), 1535 (C–N), 1445, 1430, 1330, 1280, 1180, 1165, 1105, 1070, 1025, 1010, 950, 800, 770, 705, 690. – ^{1}H NMR ($CDCl_3$): δ = 2.01 (s, 3H, CH_3), 2.67 [s, 6H, $N(CH_3)_2$], 6.80–7.52 (2 m, 10H, aromatic H), 13.19 (s, 1H, N–H···O). – ^{13}C NMR ($CDCl_3$): δ = 16.4 (C-4); 48.5 [$N(CH_3)_2$]; 107.1 (C-2); 125.9, 127.1, 127.9, 128.1, 133.2, 140.1, 142.8 (aromatic C); 165.1 (C-3); 191.0 (C-1). – MS (80 eV): *m/z* (%) = 280 (48) [M^+], 237 (12) [$M^+ - CH_3CO$], 175 (82) [$M^+ - PhCO$], 165 (33), 132 (36), 130 (61), 105 (82) [$C_6H_5CO^+$], 91 (82), 77 (100) [$C_6H_5^+$], 59 (33), 51 (33), 45 (22), 44 (99) [$N(CH_3)_2^+$], 43 (55), 42 (88), 41 (30), 40 (24), 39 (21), 32 (39), 29 (27), 27 (45).

$C_{18}H_{20}N_2O$ (280.4) Calcd. C 77.11 H 7.19 N 9.99
Found C 77.20 H 7.18 N 10.04

1-[2-(N,N-Dimethylhydrazino)-3-methyl-1-cyclopentenyl]-2,2-dimethyl-1-propanone (**4h**): According to the general procedure I 1.20 g (10 mmol) of pivaloyl chloride was treated with **3e**, prepared from 1.40 g (10 mmol) of **2e**, to afford 1.82 g (81%), b.p. 80°C (bath)/0.1 Torr, pale yellow crystals, m.p. 49–51°C. – IR (KI): $\tilde{\nu}$ = 3460 cm^{-1} (br. N–H···O), 2960, 2860, 2820, 2780, 1700 (C=O), 1660 (C=O···H), 1610, 1550 (C–N), 1480, 1470, 1450, 1390, 1365, 1320, 1305, 1280, 1210, 1190, 1170, 1065, 1015, 970, 865. – ^{1}H NMR (CCl_4): δ = 0.98–1.32 [complex, 12H, CH_3, $C(CH_3)_3$, all doubled], 1.34–2.12 (m, 4H, ring CH_2), 2.17 [s, <3H, $N(CH_3)_2$, **4B**], 2.43–2.86 (m, 1H, methine H), 2.56 [s, <3H, $N(CH_3)_2$, **4A**], 3.63–4.01 (m, 0.5H, methine H, **4B**), 10.31 (s, 0.5H, N–H···O). – ^{13}C NMR ($CDCl_3$): δ = 16.8 (CH_3); 17.0 (CH_3); 18.6 (CH_3); 26.6, 26.9, 27.4, 28.0, 29.4, 29.9, 30.5, 31.2, 32.1, 33.2, 37.7, 38.6, 39.7, 42.3, 46.1, 48.3 (ring C, **4A,B**); 47.7, 49.1 [$N(CH_3)_2$, **4A,B**]; 100.5 (C-2); 172.5, 182.8, 183.3 (C-1, **4A,B**, other isomer); 202.0, 212.7, 212.8 (C=O, **4A,B**, other isomer). – MS (80 eV): *m/z* (%) = 224 (42) [M^+], 180 (11) [$M^+ - 44$], 167 (24) [$M^+ - 57$], 140 (20), 139 (100) [$M^+ - 85$]. 125 (16), 124 (14), 122 (13), 98 (22), 96 (87), 95 (9), 94 (8), 85 (7) [$C_4H_9CO^+$], 84 (11), 82 (14), 79 (21), 72 (16), 70 (22), 69 (52), 57 (62) [$C_4H_9^+$], 55 (47), 45 (22), 44 (99) [$N(CH_3)_2^+$], 43 (30), 42 (62), 41 (58), 39 (14).

$C_{13}H_{24}N_2O$ (224.3) Calcd. C 69.59 H 10.78 N 12.49
Found C 69.42 H 10.70 N 12.37

(E)/(Z)-2-(2,2-Dimethylpropanoyl)cyclohexanone Dimethylhydrazone (**4i**): According to the general procedure I 1.2 g (10 mmol) of pivaloyl chloride was treated with **3f**, prepared from 1.4 g (10 mmol) of **2f**, to yield 1.86 g (83%) of a viscous oil, b.p. 80–90°C/0.2 Torr. – IR (neat): $\tilde{\nu}$ = 2955 cm^{-1}, 2860, 2820, 1715 (C=O), 1705 (C=O), 1630 (C=O), 1480, 1470, 1450, 1390, 1365, 1320, 1230, 1195, 1140, 1125, 1080, 1060, 1020, 980, 930. – ^{1}H NMR ($CDCl_3$): δ = 1.19 [s, 9H, $C(CH_3)_3$], 1.32–2.08 (m, 6H, 3–5-H_2), 2.20–2.50 [complex, 8H, 6-H_2, $N(CH_3)_2$], 3.82 (m, *J* = 7.5, 5.0 Hz, 1H, 2-H-2). – ^{13}C NMR ($CDCl_3$): (*E*)-**4i**: δ = 26.5 [$C(CH_3)_3$], 45.0 [$C(CH_3)_3$], 47.0 [$N(CH_3)_2$], 23.3 (C-4), 27.0 (C-5), 27.7 (C-3), 30.1 (C-6), 51.1 (C-2), 168.6 (C-1), 214.7 (C=O); (*Z*)-**4i**: δ = 26.2 [$C(CH_3)_3$], 46.5 [$N(CH_3)_2$], 27.3 (C-5), 30.7 (C-3), 34.6 (C-6), 47.3 (C-2), 170.9 (C-1). – MS (80 eV): *m/z* (%) = 224 (30) [M^+], 180 (3), [$M^+ - 44$], 167 (7) [$M^+ - 57$], 140 (24), 139 (100) [$M^+ - 85$], 124 (4), 122 (7), 110 (6), 97 (10), 96 (85) [$M^+ - 128$], 95 (8), 94 (9), 85 (4) [$C_4H_9CO^+$], 81 (10), 79 (36), 72 (7), 71 (24), 70 (13), 69 (58) [$C_5H_9^+$], 68 (7), 67 (10), 59 (6), 58 (7), 57 (45) [$C_4H_9^+$], 56 (7), 55 (34), 54 (10), 53 (6), 46 (9), 45 (7), 44 (55) [$N(CH_3)_2^+$], 43 (23) [$C_3H_7^+$], 42 (54), 41 (42), 39 (11).

$C_{13}H_{24}N_2O$ (224.3) Calcd. C 69.59 H 10.78 N 12.49
Found C 69.47 H 10.75 N 12.36

6-Methyl-2-(2-methylpropanoyl)cyclohexanone Dimethylhydrazone (**4j**): According to the general procedure I 0.50 g (5 mmol) of isobutyryl chloride was treated with **3g**, prepared from 0.77 g (5 mmol) of **2g**, to yield 0.91 g (81%) of a yellow liquid, b.p. 90–100°C (bath)/0.5 Torr. – IR (neat): $\tilde{\nu}$ = 2965 cm^{-1}, 2930, 2820, 2780, 1730 (C=O), 1710 (C=O), 1600 (C=O), 1560, 1470, 1445, 1375, 1215, 1145, 1020, 970. – **4j** was further characterized by transformation into **6j**.

5-Methyl-2-(2-methylpropanoyl)cyclohexanone Dimethylhydrazone (**4k**): According to the general procedure I 1.01 g (10 mmol) of isobutyryl chloride was treated with **3h**, prepared from 1.54 g (10 mmol) of **2h**, to afford 1.81 g (81%) of a pale yellow liquid, b.p. 100–110°C (bath)/0.05 Torr. – IR (neat): $\tilde{\nu}$ = 2970 cm^{-1}, 2930, 2855, 2820, 2785, 1705 (C=O), 1595, 1560, 1475, 1460, 1445, 1350. – **4k** was further characterized by transformation into **6k**.

2-(2,2-Dimethylpropanoyl)-5-methylcyclohexanone Dimethylhydrazone (**4l**): According to the general procedure I 1.20 g (10 mmol) of pivaloyl chloride was treated with **3h**, prepared from 1.54 g (10 mmol) of **2h**, to afford 1.83 g (82%) of a yellow liquid, b.p. 90–100°C (bath)/0.02 Torr. – IR (neat): $\tilde{\nu}$ = 2960 cm^{-1}, 2870, 2820, 1705 (C=O), 1630, 1460, 1365, 1310, 1195, 1135, 1070, 1020, 970, 955, 945, 870. – ^{1}H NMR ($CDCl_3$): δ = 1.04–1.25 [complex, 12H, $C(CH_3)_3$, CH_3, 2 isomers]; 1.32–2.14 (m, 5H, 3-, 4-H_2, 5-H);

2.18–2.43 (m, 2H, 6-H_2); 2.33, 2.34 [2 s, 6H, $N(CH_3)_2$]; 3.78–4.04 (m, 1H, 2-H). – MS (80 eV): *m/z* (%) = 238 (16) [M^+], 153 (100) [$M^+ - (CH_3)_3CCO$], 110 (63), 93 (26), 83 (16), 69 (21) [$C_5H_9^+$], 57 (44) [$C(CH_3)_3$], 44 (36) [$N(CH_3)_2^+$], 42 (30), 41 (30), 29 (30).

$C_{14}H_{26}N_2O$ (238.4) Calcd. C 70.54 H 11.00 N 11.75
Found C 70.60 H 11.06 N 11.60

3-(N,N-Dimethylhydrazino)-2-tetradecenal (**4m**): According to the general procedure I 0.74 g (10 mmol) of ethyl formate was treated with **3j**, prepared from 2.1 g (8.75 mmol) of **2j**, to afford 2.0 g (87%) of a highly viscous, yellow oil, b.p. 75–80°C/10^{-5} Torr, solid at 22°C. – IR (neat): $\tilde{\nu}$ = 3300–3150 cm^{-1} (N–H···O), 3040, 2980, 2975, 2920, 2845, 2820, 2780, 2725, 1715, 1680, 1610, 1580, 1550, 1500, 1465, 1450, 1390, 1385, 1310, 1220, 1190, 1155, 1015, 920, 880, 840, 720. – ^{1}H NMR ($CDCl_3$): δ = 0.89 (t, *J* = 5.7 Hz, 3H, CH_3), 1.27 (m, 16H, 5–11-H_2), 1.57 (m, *J* = 5.71 Hz, 2H, 12-H_2), 2.19 (t, *J* = 7.72 Hz, 2H, 4-H_2), 2.56 [s, 6H, $N(CH_3)_2$], 4.80 (d, *J* = 2.35 Hz, 1H, 2-H), 8.92 (d, *J* = 2.35 Hz, 1H, CHO), 11.25 (br. s, 1H, N–H···O). – ^{13}C NMR ($CDCl_3$): δ = 14.1 (C-13); 22.7 (C-12); 28.4, 29.3, 29.4, 29.5, 29.5, 29.6, 29.6, 29.7, 29.8, 31.2, 31.9, 34.1 (C-5–11); 39.1 (C-4); 47.0, 47.1, 48.6 [$N(CH_3)_2$], 93.5 (C-2), 185.6 (C-1). – MS (70 eV): *m/z* (%) = 270 (1) [M^+ + 1], 268 (27) [M^+], 267 (2) [M^+ – H], 253 (1) [$M^+ - CH_3$], 252 (1), 251 (2), 240 (1) [M^+ – CO], 239 (1), 237 (1), 236 (1), 227 (1), 226 (4), 225 (19), [M^+ – 43], 224 (100) [$M^+ - N(CH_3)_2$], 200 (2), 198 (2), 197 (2), 196 (4) [$M^+ - C_5H_{12}$], 194 (1), 184 (3), 183 (3), 182 (2), 180 (1), 170 (2), 169 (2), 155 (2), 154 (2), 152 (2), 142 (2), 141 (10), 140 (2), 139 (2), 138 (2), 129 (3), 128 (16) [$M^+ - C_{10}H_{20}$], 127 (2), 126 (2), 125 (2), 124 (3), 123 (2), 121 (1), 115 (3), 114 (2), 113 (4), 112 (4), 111 (4), 110 (5), 109 (5), 105 (1), 101 (3), 100 (10) [$C_5H_{12}N_2^+$], 91 (7), 96 (16), 95 (8), 94 (3), 91 (3), 87 (2), 86 (8), 85 (15), 84 (13), 83 (7), 82 (6), 81 (7), 79 (3), 72 (4), 71 (7), 70 (9), 69 (8), 68 (4), 67 (7), 60 (49) [$C_2H_8N_2^+$], 59 (15), 58 (17), 57 (17), 55 (19), 54 (4), 53 (4), 46 (7), 45 (47), 44 (57) [$N(CH_3)_2^+$], 43 (25), 42 (16), 41 (20), 39 (8).

$C_{16}H_{32}N_2O$ (268.4) Calcd. C 71.59 H 12.01 N 10.44
Found C 71.88 H 12.20 N 10.56

1-Amino-1-phenyl-1-hexen-3-one N,N-Dimethylhydrazone (**5a**): According to the general procedure I 1.13 g (10 mmol) of benzonitrile was treated with **3c**, prepared from 1.28 g (10 mmol) of **2c**, to yield 1.97 g (85%) of a yellow, highly viscous, undistillable oil. – IR (neat): $\tilde{\nu}$ = 3460 cm^{-1}, 3150 (NH_2), 3060; 3030; 2950; 2870; 2850; 2780; 1620; 1600; 1570; 1520; 1465; 1430; 1415; 1375; 1340; 1325; 1245; 1205; 1190; 1150; 1075; 1055; 1015; 1000; 995; 635. – ^{1}H NMR (CCl_4): δ = 0.98 (t, 3H, CH_3), 1.34–1.82 (m, 2H, 5-H_2), 2.34–2.67 (m, 2H, 4-H_2), 2.47 [s, 6H, $N(CH_3)_2$], 4.82 (s, 1H, 2-H), 6.84 (s, 2H, NH_2), 7.26–7.70 (m, 5H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 14.4 (C-6); 21.5 (C-5); 34.2 (C-4); 48.8 [$N(CH_3)_2$]; 92.8 (C-2); 126.1, 128.6, 128.8 (aromatic C); 152.0 (C-1); 171.0 (C-3). – MS (80 eV): *m/z* (%) = 231 (7) [M^+], 215 (3) [$M^+ - NH_2$], 172 (16), 170 (8), 158 (28), 157 (36), 140 (6) [M^+ – 91], 130 (8), 119 (50), 105 (14) [$C_6H_5CNH_2^+$], 104 (100) [$C_6H_5C{=}NH^+$], 103 (99) [$C_6H_5C{\equiv}N^+$], 91 (123), 79 (9), 78 (28), 77 (69) [$C_6H_5^+$], 76 (53), 75 (11), 70 (10), 57 (17), 52 (28), 51 (33) [$C_4H_3^+$], 50 (30), 45 (75), 44 (92) [$N(CH_3)_2^+$], 43 (38), 42 (91), 41 (93), 40 (18), 39 (29), 30 (13), 29 (68), 28 (72), 27 (34), 15 (29) [CH_3^+].

$C_{14}H_{21}N_3$ (231.3) Calcd. C 72.69 H 9.15 N 18.16
Found C 72.50 H 8.98 N 18.22

1-Amino-1-(4-bromophenyl)-4-methyl-1-penten-3-one N,N-Dimethylhydrazone (**5b**): According to the general procedure I 1.92 g (10.5 mmol) of *p*-bromobenzonitrile was treated with **3d**, prepared from 1.45 g (11.4 mmol) of **2d**, to yield 3.00 (92%) of pale yellow needles (*n*-pentane), m.p. 92–92.5°C. – IR (KBr): $\tilde{\nu}$ = 3430 cm^{-1} (NH_2), 3180–3130 (NH_2, N–H···N), 1660 (C=N). – ^{1}H NMR ($CDCl_3$): δ = 1.12 [d, *J* = 7.0 Hz, 6H, $(CH_3)_2CH$], 2.52 [s, 6H, $N(CH_3)_2$], 3.76 [m, *J* = 7.0 Hz, 1H, $(CH_3)_2CH$], 4.85 (s, 1H, 2-H), 6.22–6.77 (br. s, 2H, NH_2), 7.33–7.58 (m, 4H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 21.1 (C-5); 28.1 (C-4); 45.4, 49.1 [$N(CH_3)_2$], 89.3 (C-2); 122.9, 127.8, 127.9, 131.8, 138.7 (aromatic C); 151.5 (C-1); 175.7 (C-2). – MS (70 eV): *m/z* (%) = 312 (15) [M^+ (^{81}Br) + 1], 311 (68) [M^+ (^{81}Br)], 310 (18) [M^+ (^{79}Br) + 1], 309 (69) [M^+ (^{79}Br)], 268 (17), 267 (71) [M^+ (^{79}Br) – $N(CH_3)_2$], 266 (25), 265 (100) [M^+ (^{79}Br) – $N(CH_3)_2$], 264 (9), 263 (26), 254 (11), 253 (9), 252 (28), 251 (23), 250 (21), 249 (20), 240 (12), 238 (14), 225 (25), 224 (23), 223 (26), 222 (20), 210 (10), 208 (15), 202 (8), 199 (62), 198 (15), 197 (74), 196 (8), 195 (9), 186 (6), 185 (18), 184 (35), 183 (13), 182 (20), 181 (9), 158 (10), 157 (12) [$C_6H_4{}^{81}Br^+$], 156 (18), 155 (11) [$C_6H_4{}^{79}Br^+$], 146 (8), 144 (28), 128 (12), 127 (13), 119 (40), 118 (24), 102 (18), 101 (20), 90 (12), 89 (14), 45 (21), 44 (79) [$N(CH_3)_2^+$], 43 (31), 42 (40), 41 (25), 40 (7), 39 (8).

$C_{14}H_{20}BrN_3$ (310.2) Calcd. C 54.19 H 6.50 N 13.54
Found C 54.40 H 6.52 N 13.51

1-Amino-1-(2-naphthyl)-1-penten-3-one N,N-Dimethylhydrazone (**5c**): According to the general procedure I 1.60 g (10.5 mmol) of 2-naphthonitrile was treated with **3b**, prepared from 1.28 g (11.34 mmol) of **2b**, to yield 2.65 g (94%) of yellow needles (*n*-pentane), m.p. 67–68°C. – IR (KBr): $\tilde{\nu}$ = 3390 cm^{-1} (br. NH_2), 3200–3110 (NH_2, N–H···N), 1625 (C=N). – ^{1}H NMR ($CDCl_3$): δ = 1.22 (t, *J* = 7.0 Hz, 3H, CH_3), 2.55 (q, *J* = 7.0 Hz, 2H, CH_2), 2.56 [s, 6H, $N(CH_3)_2$], 5.06 (s, 1H, 2-H), 6.44–7.34 (br. s, 2H, NH_2), 7.34–8.00 (m, 7H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 12.8 (C-5); 25.3 (C-4); 48.9 [$N(CH_3)_2$]; 84.5 (C-2); 93.0, 124.2, 125.1, 126.5, 127.7, 128.3, 128.4, 128.7, 133.3, 136.8 (aromatic C); 152.1 (C-1); 172.1 (C-3). – MS (70 eV): *m/z* (%) = 268 (25) [M^+ + 1], 267 (100) [M^+], 252 (27) [$M^+ - CH_3$], 224 (15) [M^+ – 43], 223 (80) [$M^+ - N(CH_3)_2$], 222 (18), 221 (22), 209 (12), 208 (39) [$M^+ - (CH_3)_2NNH$], 197 (5), 196 (9), 194 (25) [$M^+ - (CH_3)_2NNHCH_2$], 193 (18) [$M^+ - (CH_3)_2NNHCH_3$], 180 (19), 179 (10), 178 (11), 170 (16), 169 (88) [$M^+ - C_5H_{10}N_2$], 168 (12), 167 (17), 166 (13), 165 (8), 155 (12), 154 (55) [$M^+ - (CH_3)_2NNHC(CH)C_2H_5$], 153 (25), 152 (14), 141 (16), 140 (13) [$M^+ - C_{10}H_7$], 139 (8), 128 (15), 127 (25) [$C_{10}H_7^+$], 126 (18), 45 (11), 44 (35) [$N(CH_3)_2^+$], 43 (12), 42 (18).

$C_{17}H_{21}N_3$ (267.4) Calcd. C 76.37 H 7.92 N 15.72
Found C 76.45 H 7.94 N 15.54

2-[Amino(4-bromophenyl)methylidene]-5-methylcyclohexanone Dimethylhydrazone (**5d**): According to the general procedure I 1.92 g (10.5 mmol) of *p*-bromobenzonitrile was treated with **3h**, prepared from 1.58 g (11.0 mmol) of **2h**, to yield 3.00 g (85%) of yellow needles (*n*-pentane/ether), m.p. 105–106°C. – IR (KBr): $\tilde{\nu}$ = 3400 cm^{-1}, 3360 (NH_2); 3250 (N–H···N); 1600 (C=N). – ^{1}H NMR ($CDCl_3$): δ = 0.92, 1.02 (2 d, 3H, CH_3); 1.34–2.66 (m, 7H, ring H); 2.53, 2.58 [2 s, 6H, $N(CH_3)_2$]; 5.44–6.44 (br. s, NH_2, H/D exchange, 83%); 12.18–14.44 (br. s, =NH, 17%); 7.16–7.67 (m, 4H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 18.0 (CH_3); 22.4, 21.92, 27.5, 28.2, 29.0, 31.0, 32.6 (C-3–6); 48.5, 48.2 [$N(CH_3)_2$]; 85.4, 97.7 (C-2); 122.0, 122.6, 128.5, 130.1, 130.5, 131.0, 131.6, 139.1 (aromatic C); 141.8, 146.9 (C-1). – MS (70 eV): *m/z* (%) = 338 (40) [M^+ (^{81}Br) + 1], 337 (73) [M^+ (^{81}Br)], 336 (55) [M^+ (^{79}Br) + 1], 335 (74) [M^+ (^{79}Br)], 322 (25) [M^+ (^{81}Br) – CH_3], 320 (26) [M^+ (^{79}Br) – CH_3], 295 (8), 294 (38), 293 (99) [M^+ (^{81}Br) – $N(CH_3)_2$], 292 (55) [M^+ (^{79}Br) – 43], 291 (100) [M^+ (^{79}Br) – $N(CH_3)_2$], 290 (20), 289 (16), 278 (12), 277 (15), 276 (12), 275 (14), 266 (8), 265 (9), 264 (10), 263 (8), 250 (10), 249 (8), 248 (9), 212 (14), 211 (10), 210 (14), 199 (15), 198 (12), 197 (20), 186 (20), 185 (23), 184 (22), 183 (40), 182 (21), 181 (24), 169 (25), 168 (12), 157 (20) [$C_6H_4{}^{81}Br^+$], 156 (25), 155 (19) [$C_6H_4{}^{79}Br^+$], 154 (30), 153 (85), 144 (10), 143 (10), 139 (9), 131

(14), 130 (18), 129 (8), 128 (10), 127 (9), 115 (10), 110 (43), 108 (12), 101 (14), 102 (23), 96 (10), 95 (20), 77 (13), 76 (14), 75 (12), 69 (25), 68 (14), 67 (13), 59 (9), 55 (12), 54 (10), 51 (14), 50 (14), 46 (10), 45 (18), 44 (58) [$N(CH_3)_2^+$], 43 (20), 42 (35), 41 (28), 39 (12).

$C_{16}H_{22}BrN_3$ (336.3) Calcd. C 57.15 H 6.59 N 12.50
Found C 57.37 H 6.50 N 12.46

3,5-Octanedione (**6a**): According to the general procedure II 1.84 g (10 mmol) of **4b** was hydrolyzed to yield 0.95 g (56%) of a colourless liquid, b.p. 80–90°C (bath)/8 Torr (ref.[54] 67–70°C/12 Torr). The spectroscopic data are in agreement with those reported in the literature[55].

2-Methyl-3,5-octanedione (**6b**): According to the general procedure II 1.98 g (10 mmol) of **4c** was hydrolyzed to give 0.98 g (63%) of a light yellow liquid, b.p. 110–120°C (bath)/16 Torr (ref.[56] 89°C/20 Torr). – IR (neat): $\tilde{\nu}$ = 3460–3010 cm^{-1} (O–H···O); 2960, 2930, 2870, 1735, 1710 (C=O, diketo form); 1610 (C=O, enol form); 1475; 1420; 1095; 935; 790. – ^1H NMR (CCl_4): δ = 0.96 (t, 3H, CH_3), 1.14 (d, 6H, 2 CH_3), 1.38–1.82 (m, 2H, 7-H_2), 1.96–2.60 (m, 3H, 6-H_2, 2-H), 3.49 (s, ≤2H, 4-H_2, diketo form), 5.42 (s, <1H, 4-H, enol form), 15.31 (s, <1H, O–H···O).

2-Methyl-3,5-hexadecanedione (**6c**): According to the general procedure II 2.8 g (9 mmol) of **4d** was hydrolyzed to yield **6c**, which was purified and characterized as its light blue copper chelate (prepared according to the general procedure III), m.p. 70–71°C. The copper chelate was further hydrolyzed (10% HCl/$CHCl_3$) to give 2.2 g (91%) of pure **6c**, b.p. 133–134°C/0.6 Torr. – IR (neat): $\tilde{\nu}$ = 3450 cm^{-1} (O–H···O, intramolecular chelation), 1595, 1555–1540 (C=O···H, 100% enol form). – ^1H NMR ($CDCl_3$): δ = 0.87 (t, 3H, CH_3), 1.13 [dd, *J* = 7.0 Hz, 6H, $CH(CH_3)_2$], 1.20–1.78 [m, 19H, $[CH_2]_9$, 2-H], 2.29 (t, *J* = 6.5 Hz, 2H, 6-H_2), 5.50 (s, 1H, 4-H, enol form), 15.29–15.96 (br. s, H/D exchange). – ^{13}C NMR: δ = 14.1, 17.8, 22.8, 23.5, 25.8, 29.1, 29.3, 29.4, 29.6, 29.7, 33.0, 38.6, 41.8, 43.7 ($[CH_2]_{10}CH_3$); 19.4 [q, $CH(CH_3)_2$]; 36.7 [d, $CH(CH_3)_2$]; 55.0 (t, C-4, diketo form); 97.0 (d, C-4, enol form); 195.0 (s, C-5); 198.7 (s, C-3); 204.6 (s, C-5); 208.3 (s, C-3). – MS (70 eV): *m/z* (%) = 268 (13) [$M^+ - H_2O$], 250 (8), 226 (14), 225 (89), 207 (14), 183 (14), 170 (5), 164 (11), 141 (13), 129 (12), 128 (100) [$C_7H_{12}O_2^+$], 113 (25), 109 (5), 100 (10), 97 (9), 95 (8), 85 (5), 85 (25), 83 (8), 81 (7), 71 (8), 71 (64), 71 (9), 70 (6), 69 (10), 67 (9), 57 (22), 56 (5), 55 (19), 55 (6), 43 (47), 43 (17), 42 (6), 41 (28), 39 (7).

$C_{17}H_{32}O_2$ (286.4) Calcd. C 76.06 H 12.02
Found C 75.92 H 12.20

1-Phenyl-1,3-hexanedione (**6d**): According to the general procedure II 2.32 g (10 mmol) of **4f** was hydrolyzed to yield 1.15 g (61%) of a light yellow liquid, b.p. 90–100°C (bath)/0.35 Torr (ref.[57] 125–128°C/2.5 Torr). – IR (neat): $\tilde{\nu}$ = 3500–3280 cm^{-1} (O–H···O), 3045, 2940, 2910, 2855, 1725 (C=O, diketo form), 1610 (C=O···H), 1475, 1465, 1290, 1190, 1175, 1125, 1115, 1045, 1020, 970. – ^1H NMR (CCl_4): δ = 0.97 (t, 3H, CH_3), 1.23–1.97 (m, 2H, 5-H_2), 2.33 (t, 2H, 4-H_2), 3.90 (s, ≤1H, 2-H_2, diketo form), 6.07 (s, <1H, 2-H, enol form), 7.13–7.57 (m, 3H, aromatic H), 7.60–8.07 (m, 2H, aromatic H), 16.20 (br. s, <1H, O–H···O).

1,2-Diphenyl-1,3-butanedione (**6e**): According to the general procedure II 1.4 g (5 mmol) of **4g** was hydrolyzed to yield **6e**, which was purified by column chromatography (SiO_2, ether) to give a mixture of colorless plates and pink needles. Attempted fractional crystallization form *n*-pentane was unsuccessful; yield 0.94 g (79%), m.p. 75–79°C (literature data for the diketo/keto-enol form: 75–80°C[58], 80–82°C[59], 76–77°C[60]; literature for the keto-enol form: 88–89°C[58]). – The IR spectral data are in agreement with those reported by House et al.[58].

1-(4-Bromophenyl)-4-methyl-1,3-pentanedione (**6f**): According to the general procedure II 1.25 g (4 mmol) of **5b** was hydrolyzed to yield 1.00 g (92%) of **6f**, which was purified and characterized as its copper chelate (prepared according to the general procedure III). The blue copper chelate, m.p. 211–212°C (MeOH), was hydrolyzed with 2 N HCl (15 ml)/MeOH (20 ml) to yield 0.80 g (74%) of **6f**, b.p. 118–120°C/0.2 Torr. – IR (neat): $\tilde{\nu}$ = 3400 cm^{-1} (O–H···O), 1710 (C=O, diketo form), 1600 (C=O···H). – ^1H NMR ($CDCl_3$): δ = 1.22 [d, *J* = 7 Hz, 6H, $CH(CH_3)_2$], 2.64 [m, *J* = 7 Hz, 1H, $CH(CH_3)_2$], 4.13 (s, ≤1H, 2-H_2, diketo form, 7%), 6.18 (s, <1H, 2-H, enol form, 92%), 7.54–7.84 (m, 4H, aromatic H), 15.67–16.57 (br. s, <1H, OH···O, H/D exchange); (CCl_4): δ = 1.00 [d, *J* = 7 Hz, 6H, $CH(CH_3)_2$], 2.35 [m, *J* = 7 Hz, 1H, $CH(CH_3)_2$], 5.80 (s, 1H, 2-H, enol form, 100%), 7.00–7.80 (m, 4H, aromatic H), 11.43–11.93 (br. s, OH···O, H/D exchange). – ^{13}C NMR ($CDCl_3$): δ = 19.4 (C-5); 37.6 (C-4); 94.1 (C-2); 182.9 (C-1); 201.4 (C-3); 127.0, 128.6, 132.0, 133.5, 134.2 (aromatic C). – MS (70 eV): *m/z* (%) = 271 (1) [M^+(^{81}Br) + 1], 270 [M^+ (^{81}Br)], 268 (15) [M^+ (^{79}Br)], 265 (95), 227 (94), 225 (95), 185 (25), 183 (68), 157 (18), 155 (19), 147 (23), 118 (18), 105 (20), 102 (28), 90 (18), 89 (19), 77 (19), 76 (29), 75 (32), 74 (15), 69 (100) [$C_4H_5O^+$], 43 (54), 42 (12), 41 (34), 39 (22).

$C_{12}H_{13}BrO_2$ (269.1) Calcd. C 53.55 H 4.87
Found C 53.75 H 4.76

$C_{24}H_{24}Br_2CuO_4$ (599.5) Calcd. C 48.06 H 4.03
Found C 48.27 H 3.92

1-(2-Naphthyl)-1,3-pentanedione (**6g**): According to the general procedure II 1.20 g (4.5 mmol) of **5c** was hydrolyzed to give 0.95 (93%) of **6g**, which gave (according to the general procedure III) a characteristic light blue copper chelate, m.p. 221–222°C ($CHCl_3$). Hydrolysis afforded 0.55 g (54%) of cream-colored crystals, m.p. 53–54°C (*n*-pentane). – IR (KBr): $\tilde{\nu}$ = 1600 cm^{-1} (C=O···H), 1550 (C=O, aromatic C=C). – ^1H NMR ($CDCl_3$): δ = 1.22 (t, *J* = 7 Hz, 3H, CH_3), 2.52 (q, *J* = 7 Hz, 2H, CH_3CH_2), 4.20 (s, ≤1H, 2-H_2, diketo form, 15%), 6.33 (s, <1H, 2-H, enol form, 85%), 7.44–8.00 (m, 6H, aromatic H), 8.44 (s, 1H, aromatic H), 16.21 (br. s, <1H, O–H···O, H/D exchange); (CCl_4): δ = 1.20 (t, *J* = 7.5 Hz, 3H, CH_3), 2.35 (q, 2H, CH_3CH_2), 6.10 (s, 1H, 2-H, enol form, 100%), 12.20 (br. s, O–H···O), H/D exchange). – ^{13}C NMR ($CDCl_3$): δ = 19.7 (C-5); 32.5 (C-4); 53.8 (C-2); 95.8 (C-2); 95.5, 98.8, 102.4, 123.2, 123.9, 126.8, 127.0, 127.8, 128.0, 128.1, 128.4, 129.3, 129.8, 132.4, 132.8, 135.7, 141.1 (aromatic C, 2 forms); 182.9 (C-1); 198.1 (C-3). – MS (70 eV): *m/z* (%) = 227 (17) [M^+ + 1], 226 (98) [M^+], 198 (14), 197 (100) [$M^+ - C_2H_5$], 156 (10), 155 (78), 129 (37), 128 (17), 127 (52), 126 (10), 99 (11).

$C_{15}H_{14}O_2$ (226.3) Calcd. C 79.62 H 6.24
Found C 80.00 H 6.30

$C_{30}H_{26}CuO_4 \cdot H_2O$ (532.1) Calcd. C 67.72 H 5.30
Found C 67.36 H 5.25

cis/trans-2-(2,2-Dimethylpropanoyl)-5-methylcyclopentanone (**6h**): According to the general procedure II 1.12 g (5 mmol) of **4h** was hydrolyzed to give 0.77 g (85%) of **6h**, b.p. 80–90°C (bath)/0.2–0.3 Torr, m.p. 53–59°C (crystal shrank at 47°C, one fraction melted at 53°C, the rest at 58–59°C). – IR (neat): $\tilde{\nu}$ = 3480–3380 cm^{-1} (O–H···O), 2960, 2880, 1750 (C=O), 1705 (C=O), 1695 (C=O···H), 1615, 1485, 1465, 1400, 1370, 1340, 1325, 1305, 1250, 1150, 1065, 1030, 990, 945, 895, 880, 850, 795, 790. – ^1H NMR (CCl_4): δ = 1.00–1.30 [2 d, 2 s, 12H, CH_3, $C(CH_3)_3$], 1.71–2.42 (m, 5H, ring H), 3.62–3.99 (m, *J* = 9.5, 8.5 Hz, 1H, 2-H). – ^{13}C NMR ($CDCl_3$): δ = 13.6 (CH_3), 25.7 [$C(CH_3)_3$], 27.2 (C-3), 30.1 (C-4), 44.0 [$C(CH_3)_3$], 45.0 (C-5), 55.6 (C-2), 213.1 [$COC(CH_3)_3$], 215.6 (C-1). – MS (80 eV): *m/z* (%) = 182 (16) [M^+], 154 (5) [M^+ – 28], 126 (13) [M^+ – 56], 125 (96) [M^+ –

57], 111 (25), 107 (13), 99 (16) [$M^+ - 83$], 98 (96) [$M^+ - 84$], 97 (71) [$M^+ - 85$], 96 (22), 85 (46) [$C_4H_9CO^+$], 84 (39), 83 (44), 79 (15), 70 (24), 69 (100) [$C_5H_9^+$], 58 (13), 57 (99) [$C_4H_9^+$], 56 (50), 55 (77), 43 (63), 42 (17), 41 (26), 39 (23).

$C_{11}H_{18}O_2$ (182.3) Calcd. C 72.49 H 9.95
Found C 72.60 H 10.15

2-(2,2-Dimethylpropanoyl)cyclohexanone (**6i**): According to the general procedure II 1.12 g (5 mmol) of **4i** was hydrolyzed to give 0.71 g (78%) of **6i**, b.p. 80°C (bath)/0.2–0.3 Torr, light yellow crystals, m.p. 25–27°C. – IR (neat): $\tilde{\nu}$ = 2945 cm^{-1}, 2875, 1720 (C=O, diketo form), 1700 (C=O, enol form), 1480, 1470, 1455, 1370, 1330, 1320, 1290, 1130, 1060, 970. – ^1H NMR ($CDCl_3$): δ = 1.16 [s, 9H, $C(CH_3)_3$], 1.56–2.21 (m, 6H, 3–5-H_2), 2.24–2.63 (m, 2H, 6-H_2), 3.81–4.14 (m, *J* = 8.3, 5.5 Hz, 1H, 2-H). – ^{13}C NMR ($CDCl_3$): δ = 23.4 (C-4), 25.8 [$C(CH_3)_3$], 27.1 (C-5), 31.0 (C-3), 41.9 (C-6), 45.0 [$C(CH_3)_3$], 57.6 (C-2), 207.9 (C-1), 212.2 [$COC(CH_3)_3$]. – MS (80 eV): *m/z* (%) = 182 (1) [M^+], 125 (32) [$M^+ - 57$], 107 (4), 105 (8), 99 (10), 98 (100) [$M^+ - C_5H_8O$], 97 (30) [$M^+ - 85$], 85 (28) [$C_4H_9CO^+$], 83 (38), 81 (8), 79 (21), 77 (8), 70 (33), 69 (39), 67 (7), 57 (99) [$C_4H_9^+$], 56 (9), 55 (29), 43 (21), 42 (7), 41 (89), 40 (8), 39 (24).

$C_{11}H_{18}O_2$ (182.3) Calcd. C 72.48 H 9.95
Found C 72.32 H 9.83

6-Methyl-2-(2-methylpropanoyl)cyclohexanone (**6j**): According to the general procedure II 1.12 g (5 mmol) of **4j** was hydrolyzed to give 0.62 g (68%) of a light yellow liquid, b.p. 80°C (bath)/0.2–0.3 Torr. – IR (neat): $\tilde{\nu}$ = 2970 cm^{-1}, 2935, 2860, 1720 (C=O), 1705 (C=O), 1595, 1460, 1410, 1380, 1360, 1340, 1305, 1255, 1220, 1160, 1085, 965, 795. – ^1H NMR ($CDCl_3$): δ = 1.13 [d, 6H, $CH(CH_3)_2$], 1.24 (d, 3H, CH_3), 1.33–2.10 (m, 4H, 4-, 5-H_2), 2.14–3.00 [m, 4H, 3-H_2, 6-H, $CH(CH_3)_2$], 3.47–3.71 (m, <1H, 2-H, diketo form), 16.68 (s, <1H, O–H···O). – ^{13}C NMR ($CDCl_3$): δ = 18.0 (CH_3), 18.7 [$CH(CH_3)_2$], 21.1 (C-4), 24.3 (C-5), 30.5 (C-3), 33.3 (C-6), 35.8 [$CH(CH_3)_2$], 104.9 (C-2), 186.8 (C-1), 204.9 [$COCH(CH_3)_2$]. – MS (80 eV): *m/z* (%) = 182 (15) [M^+], 167 (4) [$M^+ - 15$], 140 (14) [$M^+ - 42$], 139 (98) [$M^+ - 43$], 125 (14) [$M^+ - 57$], 112 (39) [$M^+ - 70$], 111 (13) [$M^+ - 71$], 98 (5), 97 (12), 93 (18), 91 (11), 84 (7), 83 (35), 81 (11), 79 (13), 77 (14), 71 (53) [$C_3H_7CO^+$], 70 (12), 69 (15), 67 (16), 56 (7), 55 (67), 53 (15), 51 (6), 43 (100) [$C_3H_7^+$], 42 (12), 41 (76), 39 (37).

$C_{11}H_{18}O_2$ (182.3) Calcd. C 72.49 H 9.95
Found C 72.10 H 10.12

5-Methyl-2-(2-methylpropanoyl)cyclohexanone (**6k**): According to the general procedure II 2.24 g (10 mmol) of **4k** was hydrolyzed to yield 1.32 g (72%) of a light yellow liquid, b.p. 70–80°C (bath)/0.2–0.3 Torr. – IR (neat): $\tilde{\nu}$ = 3480–3100 cm^{-1} (O–H···O), 2970, 2940, 2875, 1720 (C=O), 1705 (C=O), 1600, 1465, 1455, 1415, 1212, 1150, 1085, 950, 900, 870, 850. – ^1H NMR (CCl_4): δ = 0.90–1.24 [complex, 9H, 3 CH_3; d at δ = 1.11, $(CH_3)_2CH$], 1.49–2.56 (m, 7H, ring H), 2.58–3.02 [m, 1H, $CH(CH_3)_2$]. – ^{13}C NMR ($CDCl_3$): δ = 18.7 [$CH(CH_3)_2$], 21.3 (5-CH_3), 23.2 (C-4), 28.1 (C-3), 31.2 (C-6), 33.4 (C-5), 39.6 [$CH(CH_3)_2$], 104.9 (C-2), 182.7 (C-1), 204.9 [$COiCH(CH_3)_2$]. – MS (80 eV): *m/z* (%) = 182 (14) [M^+], 140 (10), 139 (100) [$M^+ - 43$], 121 (6), 112 (24), 111 (16) [$M^+ - 71$], 97 (36), 95 (14), 94 (7), 93 (20), 91 (11), 83 (25), 81 (6), 79 (9), 77 (9), 71 (57) [$C_3H_7CO^+$], 70 (9), 69 (31), 67 (9), 55 (64), 43 (94) [$C_3H_7^+$], 41 (60), 39 (26).

$C_{11}H_{18}O_2$ (182.3) Calcd. C 72.49 H 9.95
Found C 72.28 H 10.05

cis/trans-2-(2,2-Dimethylpropanoyl)-5-methylcyclohexanone (**6l**): According to the general procedure II 2.38 g (10 mmol) of **4l** was hydrolyzed to give 1.41 g (72%) of a light yellow liqud (mixture of *cis/trans* isomers), b.p. 70–80°C (bath)/0.1 Torr. On standing, the *trans* isomer crystallized and was separated and washed several times with cold *n*-pentane, m.p. 71°C. – IR (neat): $\tilde{\nu}$ = 3390 cm^{-1} (O–H···O), 2960, 2940, 2880, 1720 (C=O), 1700 (C=O), 1480, 1460, 1395, 1370, 1230, 1205, 1130, 1065, 1005, 940, 765. – ^1H NMR ($CDCl_3$): *trans*: δ = 0.87–1.25 [d, s, 12H, CH_3, $C(CH_3)_3$; s at δ = 1.16], 1.68–2.60 (m, 7H, ring H), 3.79–4.07 [dd, *J* = 10, 1H, 6 Hz, 2-H); (CCl_4): *cis/trans*: δ = 0.94–1.19 [2 s, 2 d, 12H, CH_3, $C(CH_3)_3$; 2 s at δ = 1.08, 1.15], 1.39–2.47 (m, 7H, ring H), 3.43–4.02 (m, 1H, 2-H). – ^{13}C NMR ($CDCl_3$): *trans*: δ = 22.2 (CH_3), 25.7 [$C(CH_3)_3$], 29.7 (C-4), 32.7 (C-3), 34.8 (C-5), 44.8 [$C(CH_3)_3$], 50.3 (C-6), 56.8 (C-2), 207.6 (C-1); *cis*: δ = 21.2 (CH_3), 25.8 [$C(CH_3)_3$], 28.6 (C-4), 29.3 (C-3), 33.3 (C-5), 44.6 [$C(CH_3)_3$], 48.6 (C-6), 64.4 (C-2), 207.9 (C-1). – MS (80 eV): *m/z* (%) = 196 (3) [M^+], 139 (41) [$M^+ - 57$], 121 (7), 113 (11), 112 (100), 111 (24) [$M^+ - 85$], 97 (40), 95 (17), 93 (18), 91 (9), 85 (21) [$C_4H_9CO^+$], 84 (23), 83 (32), 70 (46), 69 (26), 58 (13), 57 (44) [$C_4H_9^+$], 55 (71), 43 (31) [$C_4H_7^+$], 42 (15), 41 (99), 39 (28).

$C_{12}H_{20}O_2$ (196.3) Calcd. C 73.43 H 10.27
cis/trans: Found C 72.98 H 10.39
trans: Found C 73.32 H 10.30

2-(4-Bromobenzoyl)-5-methylcyclohexanone (**6m**): According to the general procedure II 2.68 g (8 mmol) of **5d** was hydrolyzed to give 1.20 g (51%) of a highly viscous, undistillable oil. – IR (neat): $\tilde{\nu}$ = 3450–3250 (O–H···O), 1715 (C=O), 1690 (C=O···H), 1570, 1450, 1400, 1375, 1340, 1320, 1300, 1250, 1150, 1055, 1030, 985, 940, 875, 790. – ^1H NMR ($CDCl_3$): δ = 1.00 (2 d, *J* = 6.0 Hz, 3H, CH_3), 1.30–3.00 (m, 7H, ring H), 3.70 (s, <1H, 2-H, diketo form, 88%), 7.50–8.00 (m, 4H, aromatic H), 11.98 (br. s, ≪1H, enol form, 12%, H/D exchange). – MS (70 eV): *m/z* (%) = 296 (3) [M^+ (^{81}Br)], 294 (3) [M^+ (^{79}Br)], 215 (8), 202 (11), 198 (32) [$C_6H_4{}^{81}Br$-$COCH^+$], 196 (9) [$C_6H_4{}^{79}BrCOCH^+$], 185 (100) [$C_6H_4{}^{81}BrCO^+$], 183 (100) [$C_6H_4{}^{79}BrCo^+$], 157 (23) [$C_6H_4{}^{81}Br^+$], 155 (23) [$C_6H_4{}^{79}Br^+$], 77 (13), 76 (27), 75 (21), 74 (12), 69 (35) [$C_5H_9^+$], 55 (23) [$C_4H_7^+$], 51 (11), 50 (32), 44 (7), 43 (36) [$C_3H_7^+$], 41 (31).

$C_{14}H_{15}BrO_2$ (295.2) Calcd. C 56.97 H 5.12
Found C 56.86 H 5.22

Methyl 3-(N,N-Dimethylhydrazino)-2-hexenoate (**7a**): According to the general procedure IV 5.2 g (55 mmol) of methyl chloroformate was treated with **3c**, prepared from 1.4 g (11 mmol) of **2c**, to afford 1.3 g (65%) of a light yellow liquid, b.p. 70°C/0.4 Torr. – IR (neat): $\tilde{\nu}$ = 3450–3140 cm^{-1} (N–H···O), 2960, 2870, 2820, 2775, 1740 (C=O), 1690 (C=O), 1655, 1605, 1490, 1450, 1226, 1165, 1090, 1030, 1010, 970, 910, 785, 690. – ^1H NMR (CCl_4): δ = 0.98 (t, 3H, CH_3), 1.24–1.77 (m, 2H, 5-H_2), 2.02–2.39 (m, 2H, 4-H_2), 2.56 [s, 6H, $N(CH_3)_2$], 3.56 (s, 3H, OCH_3), 3.90 (s, ≪2H, 2-H_2, keto-hydrazone form), 4.28 (s, 1H, 2-H, enehydrazino form), 8.91 (s, 1H, N–H···O). – ^{13}C NMR ($CDCl_3$): enehydrazino form: δ = 13.9 (C-6), 21.9 (C-5), 34.4 (C-4), 48.9 [$N(CH_3)_2$], 80.4 (C-2), 165.8 (C-3), 170.9 (C-1); keto-hydrazone form: δ = 13.6 (C-6), 19.8 (C-5), 36.5 (C-4), 46.8 [$N(CH_3)_2$], 47.4 (C-2), 51.8 (OCH_3), 169.7 (C-3), 171.9 (C-1). – MS (80 eV): *m/z* (%) = 186 (22) [M^+], 155 (8) [$M^+ - OCH_3$], 154 (12) [$M^+ - HOCH_3$], 142 (20) [$M^+ - N(CH_3)_2$], 126 (22), 112 (8), 110 (14), 97 (8), 84 (13), 83 (9), 72 (13), 71 (13), 70 (10), 68 (14), 59 (18) [$CH_3CO_2^+$], 58 (15), 57 (8), 56 (8), 55 (10), 46 (9), 45 (90), 44 (100) [$N(CH_3)_2^+$], 43 (54), 42 (57), 41 (36).

$C_9H_{18}N_2O_2$ (186.3) Calcd. C 58.03 H 9.74 N 15.04
Found C 58.21 H 9.61 N 14.86

Alternatively, according to the general procedure V treatment of **3c**, prepared from 1.34 g (10.5 mmol) of **2c**, with 0.95 g (10.5 mmol) of dimethyl carbonate afforded 0.90 g (46%) of **7a**.

Ethyl 3-(N,N-Dimethylhydrazino)-2-hexenoate (**7b**): According to the general procedure IV 1.20 g (10 mmol) of diethyl carbonate was treated with **3c**, prepared from 1.34 g (10.5 mmol) of **2c**, to yield 1.26 g (61%) of a yellow liquid, b.p. 90°C/0.3 Torr, 80°C (bath)/0.07 Torr. – IR (neat): $\tilde{\nu}$ = 3340–3150 (N–H···O), 3080, 2870, 2820, 2775, 1735 (C=O), 1690 (C=O), 1655, 1610, 1490, 1450, 1360, 1266, 1165, 1040, 920, 865, 785. – ^{1}H NMR (CCl_4): δ = 0.95 (t, 3H, CH_3), 1.19 (t, 3H, OCH_2CH_3), 1.30–1.78 (m, 2H, 5-H_2), 2.10–2.41 (m, 2H, 4-H_2), 2.52 [s, 6H, $N(CH_3)_2$], 3.97 (q, 2H, OCH_2), 4.23 (s, 1H, 2-H), 8.83 (s, 1H, N–H···O); ($CDCl_3$): δ = 1.00 (t, *J* = 6.0 Hz, 3H, CH_3), 1.30 (t, *J* = 6.0 Hz, 3H, OCH_2CH_3), 1.50–2.00 (m, 2H, 5-H_2), 2.30–2.60 (m, 2H, 4-H_2), 4.15 (q, *J* = 6.5 Hz, 2H, OCH_2CH_3), 4.38 (s, 1H, 2-H), 8.98 (br. s, 1H, NH, H/D exchange). – ^{13}C NMR ($CDCl_3$): enehydrazino form: δ = 14.0 (C-6), 22.0 (C-5), 34.5 (C-4), 48.9 [$N(CH_3)_2$], 81.1 (C-2), 165.5 (C-3), 170.5 (C-1); keto-hydrazone form: δ = 13.7 (C-6), 14.2 (OCH_2CH_3), 19.7 (C-5), 36.7 (C-4), 46.7 [$N(CH_3)_2$], 47.4 (C-2), 60.6 (OCH_2CH_3), 169.1 (C-3). – MS (80 eV): *m/z* (%) = 200 (6) [M^+], 156 (12) [M^+ – $N(CH_3)_2$], 155 (8) [M^+ – 45], 154 (7), 126 (14), 110 (13), 97 (7), 96 (8), 86 (6), 84 (8), 83 (7), 73 (12) [$CO_2C_2H_5^+$], 72 (11), 71 (7), 68 (10), 67 (7), 59 (9), 58 (7), 54 (7), 45 (7) [$C_2H_5O^+$], 44 (100) [$N(CH_3)_2^+$], 43 (98), 42 (41), 41 (37), 40 (7), 39 (9).

$C_{10}H_{20}N_2O_2$ (200.3) Calcd. C 59.97 H 10.07 N 13.99
Found C 60.07 H 10.14 N 13.92

Methyl 3-(N,N-Dimethylhydrazono)-2-hexenedithioate (**7c**): According to the general procedure IV 1.53 g (10 mmol) of carbon disulfide was treated with **3c**, prepared from 1.28 g (10 mmol) of **2c**, followed by addition of 1.56 g (11 mmol) of iodomethane at –50°C to afford 2.2 g (100%) of crude **7c** as a highly viscous oil, which on distillation at 60–80°C (bath)/0.01 Torr gave 1.94 (89%) of **7c** as yellow crystals, m.p. 52°C. – IR (KI): $\tilde{\nu}$ = 2955 cm^{-1}, 2925, 2865, 2820, 2785, 2200, 1580, 1505, 1460, 1450, 1430, 1360, 1305, 1270, 1245, 1225, 1155, 1085, 1055, 880, 770, 700. – ^{1}H NMR (CCl_4): δ = 1.00 (t, 3H, CH_3), 1.40–1.86 (m, 2H, 5-H_2), 2.34–2.78 [complex, 12H, 4-H_2, $N(CH_3)_2$ SCH_3], 2.52 (s, 3H, SCH_3), 2.67 [s, 6H, $N(CH_3)_2$], 6.03 (s, 1H, 2-H), 14.16 (s, 1H, S–H···N). – ^{13}C NMR ($CDCl_3$): δ = 14.1 (C-6), 17.0 (SCH_3), 22.1 (C-5), 35.0 (C-4), 48.9 [$N(CH_3)_2$], 106.2 (C-2), 165.8 (C-3), 179.0 (C-1).

$C_9H_{18}S_2$ (218.4) Calcd. C 49.70 H 8.33 N 12.75
Found C 49.59 H 8.31 N 12.83

3-(N,N-Dimethylhydrazino)-N-phenyl-2-hexenethioamide (**8a**): According to the general procedure IV 1.35 g (10 mmol) of phenyl isothiocyanate was treated with **3c**, prepared from 1.28 g (10 mmol) of **2c**, to yield 2.68 g (100%) of crude **8a**, which crystallized in the refrigerator (ca. 7°C). The product was washed several times with *n*-pentane to afford 2.52 g (96%) of lemon-yellow crystals, m.p. 92.5–93.5°C. – IR (KBr): $\tilde{\nu}$ = 3600–3400 cm^{-1} (NH), 3340–3120 (N–H···S), 2970, 2880, 2820, 2705, 1585, 1510, 1490, 1455, 1320 (C=S), 1210 (C=S···H), 1170, 1140, 1090, 1075, 1030, 1020, 940, 910, 880, 865, 775, 750, 700. – ^{1}H NMR (CCl_4/$CDCl_3$): δ = 0.94 (t, 3H, CH_3), 1.30–1.71 (m, 2H, 5-H_2), 2.27 (t, 2H, 4-H_2), 2.64 [s, 6H, $N(CH_3)_2$], 5.18 (s, 1H, 2-H), 7.09–7.49 (m, 5H, aromatic H), 7.78 (s, 1H, N*H*C_6H_5), 12.37 (s, 1H, N–H···S). – ^{13}C NMR ($CDCl_3$): δ = 14.4 (C-6); 21.5 (C-5); 34.2 (C-4); 48.8 [$N(CH_3)_2$]; 92.8 (C-2); 124.9, 125.7, 129.1, 139.4 (aromatic C); 152.0 (C-1), 171.0 (C-3). – MS (800 eV): *m/z* (%) = 263 (29) [M^+], 230 (13) [M^+ – SH], 229 (9) [M^+ – H_2S], 219 (28) [M^+ – $N(CH_3)_2$], 190 (7), 186 (7) [M^+ – C_6H_5], 128 (6), 118 (6), 117 (7), 93 (6), 77 (26) [$C_6H_5^+$], 58 (21), 51 (6), 45 (12), 44 (29) [$N(CH_3)_2^+$], 43 (35), 42 (19), 41 (12), 40 (12), 39 (6), 32 (100) [S^+].

$C_{14}H_{21}N_3S$ (263.4) Calcd. C 63.85 H 8.02 N 15.87
Found C 63.83 H 8.04 N 15.95

3-(N,N-Dimethylhydrazino)-N-phenyl-2-butenamide (**8b**): According to the general procedure IV 1.79 g (15 mmol) of phenyl isocyanate was treated with **3a**, prepared from 1.50 g (15 mmol) of **2a**, to afford 2.50 g (76%) of colorless crystals, m.p. 160–161°C (acetone). – IR (KBr): $\tilde{\nu}$ = 3285 cm^{-1} (NH); 3195 (N–H···O); 3085, 3015 (aromatic C–H), 1710 [C=O, (*E*)-**8A**], 1640 [C=O···H, (*Z*)-**8A**], 1590 (aromatic C=C), 1600. – ^{1}H NMR ($CDCl_3$): δ = 1.86 (s, 3H, CH_3); 2.47, 2.56 [2 s, 6H, $N(CH_3)_2$, (*E*)/(*Z*)-**8A**], 3.87 (s, 1H, 2-H), 6.93–7.70 (m, 5H, aromatic H), 9.93 (br. s, 1H, NH, H/D exchange), 12.00 (br. s, 1H, N–H···O, H/D exchange). – ^{13}C NMR ($CDCl_3$): δ = 16.9, 19.3 (2 q, CH_3, (*E*)/(*Z*)-**8A**]; 47.0, 48.1, 48.4 [3 q, $N(CH_3)_2$, (*E*)/(*Z*)-**8A, B**]; 83.6 (d, C-2); 95.1, 119.6, 120.0, 120.2, 120.7, 123.2, 124.1, 124.5, 124.7, 128.1, 128.9, 129.1, 129.3, 129.7, 137.7, 138.6, 138.7, 139.5, 153.5 (aromatic C, (*E*)/(*Z*)-**8A, B**); 162.4, 164.0, 165.3 (3 s, C-3, (*E*)/(*Z*)-**8A, B**); 167.4, 169.5, 172.0 (3 s, C-1, (*E*)/(*Z*)-**8A, B**). – MS (70 eV): *m/z* (%) = 220 (1) [M^+ + 1], 219 (11) [M^+], 176 (4) [M^+ – $C_2H_5N_2$], 127 (60), 126 (67), 120 (9.2), 119 (100), 116 (11), 100 (7), 99 (7), 97 (12), 94 (5), 93 (60), 92 (13), 91 (47), 85 (9), 77 (16) [$C_6H_5^+$], 69 (9), 66 (15), 65 (19), 64 (31), 63 (12), 58 (20), 57 (9), 56 (17), 45 (10), 44 (45), 42 (23), 41 (20), 40 (9), 39 (21).

$C_{12}H_{17}N_3O$ (219.3) Calcd. C 65.73 H 7.81 N 19.16
Found C 65.80 H 7.65 N 19.00

A diacylated product with R^2 = CONHPh (<1%) and the empirical formula $C_{19}H_{22}N_4O_2$ could also be detected (MS).

$C_{19}H_{22}N_4O_2$ Calcd. 338.1743 Found 338.1749 (HRMS)

3-(N,N-Dimethylhydrazino)-N-phenyl-2-hexenamide (**8c**): According to the general procedure IV 1.25 g (10.5 mmol) of phenyl isocyanate was treated with **3c**, prepared from 1.34 g (10.5 mmol) of **2c**, to yield 1.85 g (71%) of colorless crystals, m.p. 165–166°C (acetone). – IR (KBr): $\tilde{\nu}$ = 3300 cm^{-1} (NH); 3120 (N–H···O); 3060, 3040 (aromatic C–H), 1705 [C=O, (*E*)-**8A**]; 1650 [C=O···H, (*Z*)-**8A**]; 1590 (C=C). – ^{1}H NMR ($CDCl_3$): δ = 0.93 (t, *J* = 6.2 Hz, 3H, CH_3), 1.44–1.91 (m, 2H, 5-H_2), 2.41–2.78 (m, ≪2H, 4-H_2, 2-H_2, keto-hydrazone form), 2.51 [s, 6H, $N(CH_3)_2$], 5.25 (s, 1H, 2-H), 6.95–7.33 (m, 5H, aromatic H), 7.84 (br. s, 1H, NH, H/D exchange), 9.78–10.87 (br. s, 1H, N–H···O, H/D exchange). – ^{13}C NMR ($CDCl_3$): δ = 13.8, 14.5 (2 q, C-6, 2 isomers); 19.9, 22.9 (2 t, C-5, 2 isomers); 32.5, 36.4 (2 t, C-4, 2 isomers); 48.0, 48.8, 49.9 [3 q, $N(CH_3)_2$, (*E*)/(*Z*)-**8A, B**]; 95.2 (1 d, C-2); 119.6, 119.7, 120.5, 120.6, 123.1, 125.1, 125.3, 128.8, 129.2, 129.3, 129.4, 129.7, 137.5, 138.7, 138.8 (aromatic C, 3 isomers); 165.8 (s, C-3); 166.1 (s, C-1). – MS (70 eV): *m/z* (%) = 247 (20) [M^+], 212 (15), 203 (11), 181 (44), 156 (7), 155 (79), 154 (41), 126 (15), 120 (7), 119 (60), 113 (10), 112 (16), 110 (12), 94 (9), 93 (100) [$C_6H_7N^+$], 92 (12), 91 (22), 84 (5), 77 (14), 66 (13), 65 (11), 64 (11), 51 (6), 45 (8), 44 (37), 43 (7), 41 (7), 39 (6).

$C_{14}H_{21}N_3O$ (247.3) Calcd. C 67.98 H 8.56 N 16.99
Found C 67.80 H 8.62 N 17.25

A diacylated product with R^2 = CONHPh and the empirical formula $C_{21}H_{26}N_4O_2$ could also be detected (MS).

$C_{21}H_{26}N_4O_2$ Calcd. 366.2056 Found 366.2066 (HRMS)

2-(N,N-Dimethylhydrazono)cyclohexanecarbonitrile (**9a**): According to the general procedure IV 1.96 g (10 mmol) of cyanogen bromide was treated with **3f**, prepared from 1.40 g (10 mmol) of **2f**, to afford 1.56 g (94%) of a colorless liquid. – IR (neat): $\tilde{\nu}$ = 3025 cm^{-1}, 2950, 2870, 2840, 2810, 2760, 2250 (C≡N), 1460, 1370, 1190, 1145, 1080, 1020, 960. – ^{1}H NMR ($CDCl_3$): δ = 1.45–2.20 (m, 4H, 4-, 5-H_2), 2.25 (m, 2H, 3-H_2), 2.46 [s, 6H, $N(CH_3)_2$], 2.6 (m, 2H, 6-H_2), 3.2 (dd, *J* = 7.5, 6.0 Hz, 1H, 1-H). – MS (eV): *m/z* (%) = 165 (36) [M^+], 151 (22), 150 (24), 140 (7), 139 (10) [M^+ – C≡N],

136 (14), 123 (39), 122 (15), 121 (24) [$M^+ - N(CH_3)_2$], 108 (18), 96 (83), 95 (13), 94 (69) [$M^+ - C_3H_7N_2$], 86 (10), 84 (7), 83 (7), 82 (8), 81 (7), 80 (7), 79 (11), 69 (11), 68 (8), 67 (25), 59 (35), 58 (10), 576 (10), 55 (15), 56 (18), 55 (11), 54 (11), 46 (8), 45 (35), 44 (100) [$N(CH_3)_2^+$], 43 (36), 42 (53), 41 (35), 39 (22).

$C_9H_{15}N_3$ (165.1) Calcd. C 65.35 H 9.15 N 25.50
Found C 65.70 H 9.35 N 25.20

2-(N,N-Dimethylhydrazono)cyclopentanecarbonitrile (**9b**): According to the general procedure IV 1.06 g (10 mmol) of cyanogen bromide was treated with 1.26 g (10 mmol) of cyclopentanone *N,N*-dimethylhydrazone to yield 0.70 g (46%) of a colorless liquid. – IR (neat): $\tilde{\nu}$ = 3015 cm^{-1}, 2950, 2875, 2845, 2805, 2765, 2260 (C≡N), 1610 (C=N), 1460, 1380, 1185, 1150, 1085, 1025, 954. – ^1H NMR ($CDCl_3$): δ = 1.4–2.0 (m, 2H, 4-H_2); 2.15–2.30 (m, 2H, 5-H_2), 2.4 (m, 2H, 3-H_2), 2.6 [s, 6H, $N(CH_3)_2$], 3.4 (m, 1H, 1-H). – MS (70 eV): *m/z* (%) = 152 (3) [M^+ + 1], 151 (22) [M^+], 150 (9), 149 (3), 148 (2), 140 (3), 136 (6) [$M^+ - CH_3$], 126 (4), 125 (22) [$M^+ - CN$], 124 (4), 123 (7), 122 (2), 121 (3), 120 (2), 110 (4), 109 (9), 108 (11), 107 (27) [$M^+ - N(CH_3)_2$], 106 (4), 99 (3), 98 (2), 97 (6), 86 (13), 85 (5), 84 (20), 83 (26), 82 (16), 81 (7), 80 (11), 79 (5), 72 (5), 71 (4), 70 (5), 69 (7), 68 (11), 67 (9), 66 (5), 65 (7), 70 (5), 59 (17), 58 (9), 57 (5), 56 (7), 55 (13), 54 (13), 53 (9), 52 (7), 45 (21), 44 (100) [$N(CH_3)_2^+$], 43 (40), 42 (49), 41 (26), 40 (7), 39 (13).

$C_8H_{13}N_3$ (151.2) Calcd. C 63.55 H 8.67 N 27.78
Found C 63.40 H 8.70 N 27.90

CAS Registry Numbers

2a: 13483-31-3 / **2b**: 5758-05-4 / **2c**: 28236-86-4 / **2d**: 28236-87-5 / **2e**: 69362-41-0 / **2f**: 10424-93-8 / **2g**: 5758-08-7 / **2h**: 69362-42-1 / (*E*)-**2j**: 137919-53-0 / (*Z*)-**2j**: 137919-54-1 / **2** (R^1 = Me R^2 = Ph): 4836-61-7 / **4a**: 137919-55-2 / **4b**: 137919-56-3 / **4c**: 137919-57-4 / **4d** (tautomer 4A): 137919-58-5 / **4d** (tautomer 4C): 137919-89-2 / **4e**: 137919-59-6 / **4f**: 137919-60-9 / **4g**: 137919-61-0 / **4h** (tautomer 4A): 69362-47-6 / *cis*-**4h** (tautomer 4B): 137919-90-5 / *trans*-**4h** (tautomer 4B): 138050-83-6 / (*E*)-**4i**: 137919-62-1 / (*Z*)-**4i**: 137919-63-2 / **4j**: 137919-64-3 / **4k**: 137919-65-4 / **4l**: 137919-66-5 / **4m**: 137919-67-6 / **5a**: 137919-68-7 / **5b**: 137919-69-8 / **5c**: 137919-70-1 / **5d** (tautomer 5A): 137919-94-9 / **5d** (tautomer 5B): 137919-71-2 / **6a**: 137919-72-3 / **6b** (tautomer 6A): 69362-50-1 / **6b** (tautomer 6B): 137919-95-0 / **6c** (tautomer 6A): 137919-96-1 / **6c** (tautomer 6B): 137919-73-4 / **6c** (Cu chelate): 137919-91-6 / **6d** (tautomer 6A): 5331-13-5 / **6d** (tautomer 6B): 137919-74-5 / **6e**: 137919-75-6 / **6f** (tautomer 6A): 137919-97-2 / **6f** (tautomer 6B): 137919-76-7 / **6f** (Cu chelate): 137919-92-7 / **6g** (tautomer 6A): 137919-98-3 / **6g** (tautomer 6B): 137919-77-8 / **6g** (Cu chelate): 137919-93-8 / *cis*-**6h**: 69362-51-2 / *trans*-**6h**: 69362-54-5 / **6i** (tautomer 6A): 41043-87-2 / **6i** (tautomer 6B): 137919-99-4 / **6j**: 69362-52-3 / **6k**: 137919-78-9 / *cis*-**6l**: 69362-53-4 / *trans*-**6l**: 69362-55-6 / **6m** (tautomer 6A): 137919-79-0 / **6m** (tautomer 6B): 137920-00-4 / **7a** (tautomer 7A): 137919-80-3 / **7a** (tautomer 7B): 137920-01-5 / **7b** (tautomer 7A): 137919-81-4 / **7b** (tautomer 7B): 137920-02-6 / **7c**: 137919-82-5 / **8a**: 137919-83-6 / (*E*)-**8b** (tautomer 8A): 56582-22-0 / (*Z*)-**8b** (tautomer 8A): 56582-21-9 / **8b** (tautomer 8B): 56582-23-1 / (*E*)-**8c** (tautomer 8A): 137919-84-7 / (*Z*)-**8c** (tautomer 8A): 137919-85-8 / **8c** (tautomer 8B): 137919-86-9 / **9a**: 137919-87-0 / **9b**: 137919-88-1

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