

Metallated Ketenimines: Quinazoline Derivatives from Base Induced Dimerization of *N*-Phenyldiethylketenimine. An Experimental and Theoretical Study

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Abstract: Deprotonation of *N*-phenyl-diethylketenimine **1** may be achieved by surplus strong organic base (2,2,6,6-tetramethylpiperidine, *n*-butyllithium, and potassium *tert*.butoxide in *tert*.butylmethyl ether). The resulting organometallic suspension is investigated by means of trapping reactions using trimethylacetyl chloride and dimethyl disulfide as electrophiles. From the structures of the trapping products obtained for the first step of the reaction sequence metallation at an aromatic *ortho* position is deduced. The methylene protons are not affected in the deprotonation. Addition of a second ketenimine **1** leads after ring closure to the heterocyclic anion **9**, which is trapped by the electrophiles, yielding the quinazoline derivatives **2-7**. The reaction sequence is interpreted in terms of a kinetically accelerated metallation. Semiempirical calculations (MNDO, PM3) of the gas phase acidities of *N*-phenyl-diethylketenimine **1** support this analysis. Additionally, the quantum chemical results for the optimized structures of the intermediate monomeric lithium compounds **10** and **11** are discussed.

Ketenimines are very useful building blocks in organic synthesis and have been widely applied, mainly in heterocyclic chemistry.^{3,4,5} As part of an ongoing organometallic project we are interested in possible metallations of ketenimines in order to activate these polyfunctional species for unusual reaction sequences.⁶ In principle, deprotonations from stable, trialkyl substituted ketenimines may either take place in the α -position of a *N*-alkyl group, or at an alkyl group attached to the β -carbon atom of the ketenimine moiety. In view of metallations of ketenimines until recently attention was directed mainly towards the metallation at the nitrogen atom of ketenimines (often by deprotonation of the appropriate nitriles);⁷ there are only very few reports on β -carbon-metallated ketenimines.⁸

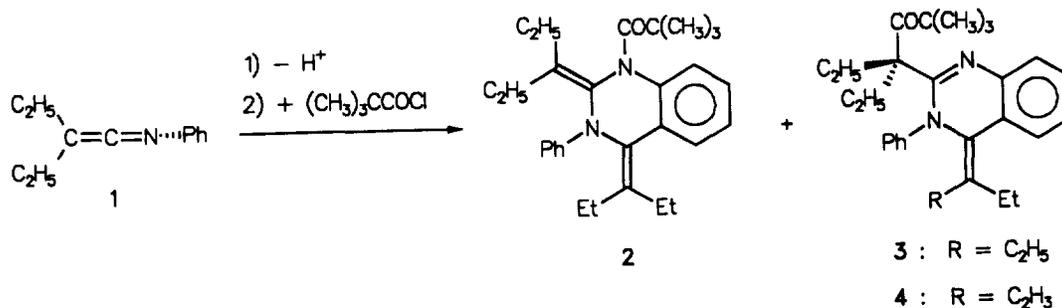
In a previous paper⁶ we reported on our investigations of metallation reactions taking place at the *N*-alkyl group of *N*-isopropyl-diphenylketenimine. Now, we investigate the behavior of *N*-phenyl-diethylketenimine (**1**) towards strong organic bases. For reasons of accessibility and stability, we have chosen **1**, which was previously unknown, for our investigations; with regard to our goal, it is important that **1** has no hydrogen atom at the β carbon atom, which may be subject to vinylic metallation.⁸ In principle, **1** offers two sites for deprotonation: as a consequence of a deprotonation at one of the methylene groups of the two ethyl moieties one would expect the formation of an allylanion, which has an imino function at the *sp*-hybridized carbon atom; alternatively, metallation may also be possible at one of the *ortho* positions of the phenyl substituent. We have investigated the course of

the deprotonation indirectly by trapping reactions, which allow to disclose the sequence of the primary reaction steps. Besides the experimental results we also present theoretical data regarding the acidity of such ketenimines and of the structures of the corresponding lithiated species (calculated for the gas phase).

N-Phenyl-diethylketenimine (**1**), which is accessible from 2-ethylbutyric acid in four steps (20.5 % yield overall), was successfully deprotonated using a mixture of 2 eq. of 2,2,6,6-tetramethylpiperidine (HTMP), 2 eq. of *n*-butyllithium and 2 eq. of potassium *tert*.butoxide⁹ using *tert*.butylmethyl ether as solvent.^{10,11} The same superbasic mixture, which is essentially a lithium/potassium 2,2,6,6-tetramethylpiperidide, was previously used in our investigations on the deprotonation of a *N*-alkylketenimine⁶ in order to ensure complete deprotonation; for steric reasons, such bases are sufficiently non-nucleophilic to avoid attack at the α carbon atom of the ketenimine.⁶ The deprotonations were performed at -78°C - -20°C yielding a deep red suspension of the organometallic intermediates; subsequently, the trapping reactions, using trimethylacetyl chloride and dimethyl disulfide as electrophiles were carried out at -78°C . Trapping is also possible using methanol as proton source; however, we were not able to separate the resulting mixture of three products. Besides spectroscopic data, two X-ray structure determinations provide complete evidence for the composition and structure of the trapping products.

Trapping with Trimethylacetyl Chloride

Treatment of the suspension of the organometallic intermediates with trimethylacetyl chloride at -78°C yields a crude mixture of three, hitherto unknown quinazoline derivatives **2-4** (ca. 80% according to ¹H NMR integration). Subsequent column chromatography and then HPLC allowed the isolation of the three compounds in rather moderate yield (**2**: 14%; **3**: 7%; **4**: 5%).



^1H and ^{13}C NMR techniques (including carbon proton chemical shift correlation with polarization transfer via the long range couplings) support the structures of these heterocyclic compounds. Furthermore, the structure of **2** was confirmed by X-ray crystallography (Fig. 1). Interesting is the pronounced boat shape structure of the heterocycle of the bicyclic system, which is mainly a consequence of heavy steric interaction. **2** shows two strongly sp^3 hybridized nitrogen atoms (sum of angles for N1=351.4°, for N9 = 345.3°), whereas the carbon atoms C8 (sum of angles = 359.5°) and C10 (sum of angles = 360°) are strictly planar, due to the exocyclic double bonds. **2** and **3** are regioisomeric and result from an attack of the electrophile at the ambident intermediate anion on nitrogen and on carbon, resp. **4** is an elimination product from **3**; it may originate from a second metallation at one of the two methylene groups, activated by the neighborhood of the heterocyclic nitrogen atom, followed by β -hydride elimination.

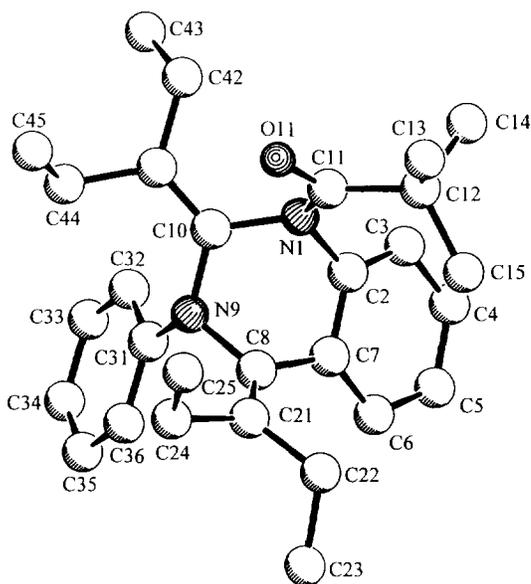
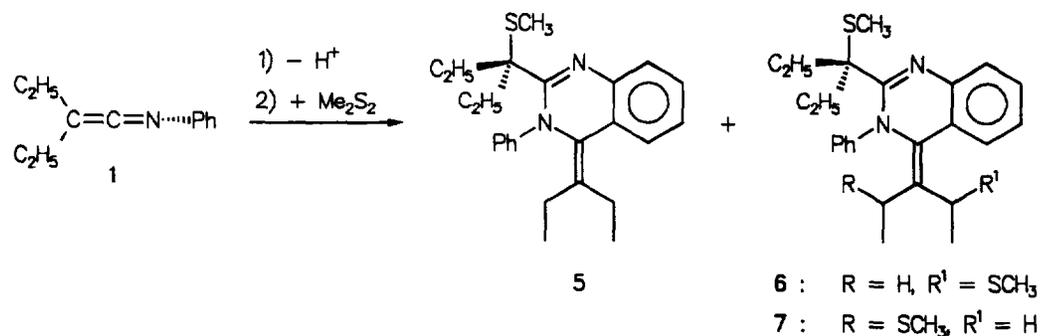


Figure 1. SCHAKAL-Plot¹² of **2** with crystallographic numbering

Trapping with Dimethyl Disulfide

The addition of dimethyl disulfide to the suspension of the organometallic intermediates yields after hydrolytic work up and HPLC a pure fraction of compound **5** (21%) and a second fraction containing a 2:1 mixture of **6** and **7** (together 29%), which proved to be not separable. All three compounds **5-7** contain the same quinazoline skeleton as **2-4**, now with a varying number of methyl sulfide groups, obviously resulting from multiple metallation/addition reactions.



The composition and the structure of the products is easily established from the 1H - and ^{13}C NMR spectra. Additionally, an X-ray structure determination of **5** (Fig. 2) offers further insight into the conformational properties of these compounds. The heterocyclic ring is by no means planar; especially nitrogen atom N10 is shifted out of the plane. Nitrogen N10 is sp^3 hybridized (sum of angles = 343.0°) and the phenyl substituent adopts the axial position, obviously for steric reasons.

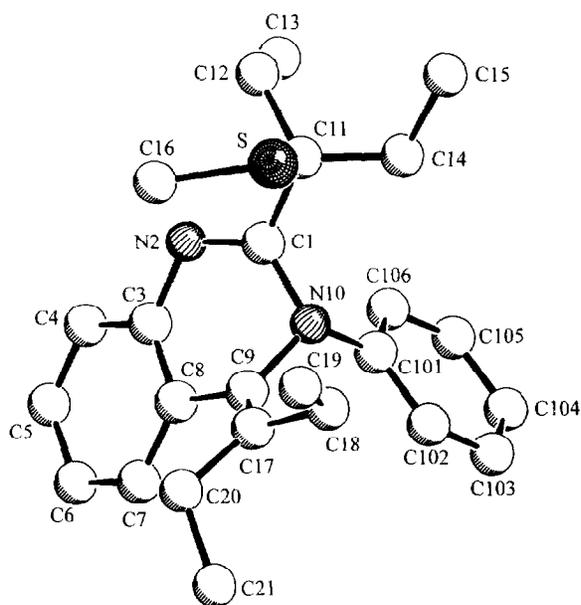
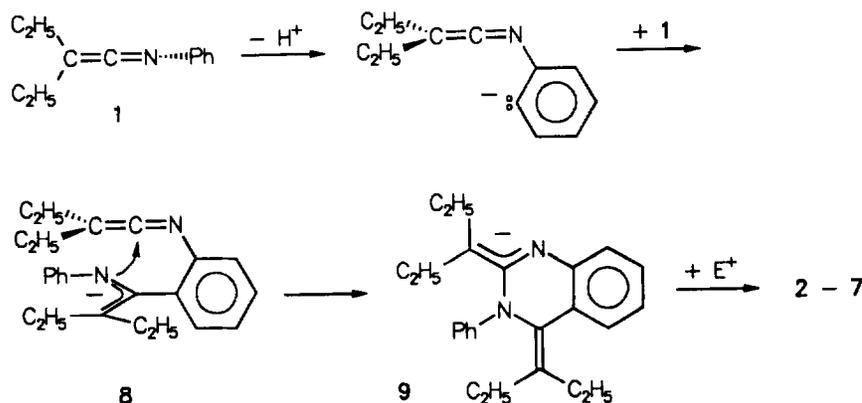


Figure 2. SCHAKAL-Plot¹² of **5** with crystallographic numbering

Mechanistic Considerations

The nature of the isolated products **2-7** suggests a common, general pathway for their formation: obviously, the *N*-phenyl substituent of the ketenimine **1** is involved into the C-C bond formation, leading to the dimeric products. We therefore suggest as the first deprotonation step of the reaction sequence a deprotonation at one of the *ortho* positions of the phenyl substituent. Such *ortho* deprotonations are well known, especially for donor-substituted aryls, e.g. phenol ethers, anilines.¹³ They proceed often unusually fast, a fact, which was explained by the "complex induced proximity effect" (CIPE)¹⁴; theoretical calculations have clarified the reasons of the "kinetically enhanced metallation" further, emphasizing the role of Lewis bases for lithium complexation in the transition state.¹⁵ At this stage of the reaction, the ethyl groups are not yet involved.



The resulting *ortho*-metallated phenyl moiety is electrophilically attacked by a second molecule of the starting material **1**, yielding the 1-azaallyl anion system **8**, which subsequently closes the quinazoline ring system giving the intermediate **9**. All isolated trapping products **2-7** are easily explained by this intermediate, which again is a 1-azaallyl anion. Eventually, a second metallation and trapping reaction may take place, explaining the formation of **6** and **7**. As discussed above, compound **4** may also be considered to be the result of a second metallation and a subsequent β -hydride elimination. The formation of 3,4-dihydroquinazolines from *N*-phenyl-ketenimines was observed earlier by M.W.Barker and J.D.Rosamond;^{4b} after heating of *N*-phenyl-dimethyl-ketenimine to 125°C for one week they obtained a mixture of 76% dimeric, 20% trimeric and 4% polymeric material. On the basis of spectroscopic data they assigned a 3,4-dihydroquinazoline structure to the dimeric product. Iminoazetidines were formed from *N*-alkyl ketenimines.^{4a} Similarly, J.Y.Becker et al. obtained varying mixtures of different 3,4-dihydroquinazoline derivatives by anodic oxidation of triaryl ketenimines.¹⁶ Our base induced dimerizations obviously proceed under very mild and well controlled conditions and offer the possibility of preparative application.

Quantum Chemical Results

The observed course of the metallation reaction (preferred aromatic metallation) most certainly is not governed by thermodynamic, but by kinetic factors.^{14,15} Nevertheless, we were interested in the structures and thermodynamic properties of the anions and organometallic species, which may possibly be involved in the reaction sequence. We have used the two semiempirical methods MNDO¹⁷ and PM3¹⁸, for which lithium parameters are available; they were implemented into the MOPAC 6 program package.¹⁹ For the deprotonation process of **1** (i.e. going from the gas phase ketenimine **1** to the corresponding anion) both methods calculate much lower heats of reactions for the deprotonation from a methylene group (MNDO: 363.9 kcal/mol; PM3: 359.2 kcal/mol). The deprotonation from the *ortho*-phenyl position is much more endothermic (MNDO: 391.1 kcal/mol; PM3: 381.6 kcal/mol). These data are in agreement with a kinetically controlled deprotonation reaction in the experimentally studied system. The deprotonation of 1,1-dimethylallene as an all carbon analogue to **1** yielding the 2-methyl-3-methylene-allylanion is predicted to afford similar energies (MNDO: 381.2 kcal/mol; PM3: 382.7 kcal/mol).

The best structures of the monomeric lithiated species in the gas phase obtained by complete geometry optimization are depicted in Fig. 3 and 4. Whereas the MNDO method gives a slightly better heat of formation for the *ortho*-lithium derivative **10-MNDO** ($\Delta H_f = 21.36$ kcal/mol), compared to the methylene metallation product **11-MNDO** ($\Delta H_f = 23.18$ kcal/mol), PM3 significantly prefers the later **11-PM3** ($\Delta H_f = 63.06$ kcal/mol versus 69.77 kcal/mol for the aryl lithium isomer **10-PM3**). MNDO and PM3 disagree in the prediction of the structure of the best *ortho*-lithiated system **10** (Fig. 3): according to MNDO, the *ortho*-lithium derivative gains much stability from interactions with the π -orbitals of the C=C double (**10-MNDO**); on the other hand, PM3, according to our experience, balances interactions of lithium atoms to carbon versus hetero atoms better; thus, we find in the best PM3 structure a strong interaction between the lone pair at nitrogen and the lithium atom in the *ortho* position (**10-PM3**). We consider PM3 to be more reliable in such calculations.

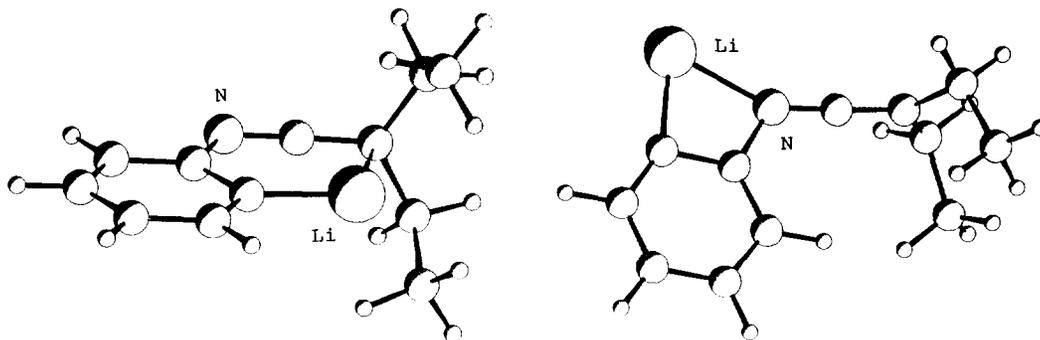


Figure 3. MNDO (left) and PM3 (right) optimized structure of the *ortho*-lithiated *N*-phenyl-diethylketenimine **10-MNDO** and **10-PM3**.

However, both methods agree in the general structural features for the systems lithiated at a methylene group **11** (Fig. 4): this form is best understood as a 1-aza-2-lithio-butadiene, with additional lithium interaction to one of the *ortho*-carbon atoms of the phenyl ring and to a terminal methyl group. The lone pair at nitrogen is only weakly involved in lithium coordination.

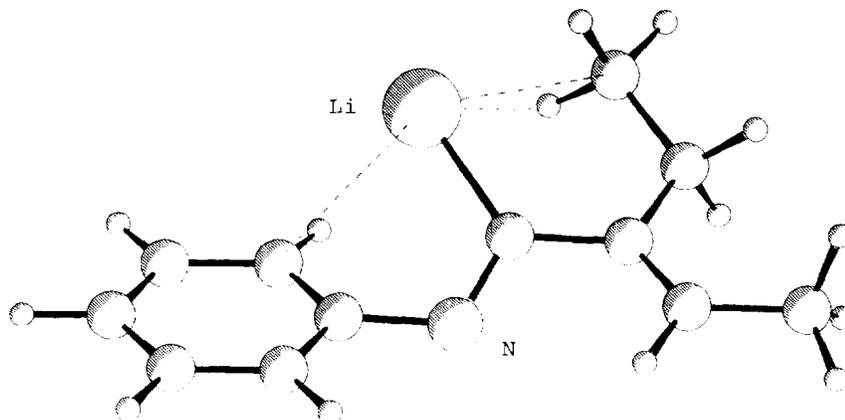


Figure 4. PM3 optimized structure of the methylene-lithiated *N*-phenyl-diethylketenimine **11-PM3**. MNDO gives a rather similar type of structure.

Conclusion

In this study, we have reported the results of metallation reactions of *N*-phenyl-diethylketenimine (**1**) using very strong organic bases. The main reaction pathway, which was deduced from the trapping products, is the kinetically enhanced *ortho* metallation at the phenyl substituent, which opens the possibility for an attack of a second ketenimine leading to quinazoline anions; they have been trapped successfully by trimethylacetyl chloride and dimethyl disulfide. The course of the reaction most probably is governed by kinetic control, as indicated by results of semiempirical quantum chemical calculations. The base induced formation of the heterocyclic systems proceeds under much milder conditions, compared to previous ketenimine dimerization reactions.^{4b,16} To abstract protons from alkyl groups at the β -carbon atom of the ketenimine, *N*-substituents without acidic hydrogen atoms are required. Alternatively, lithium free potassium amide bases may be better suited to avoid the aromatic *ortho* metallation.¹¹ Further studies are aimed towards the direct or indirect detection of the resulting unusual imino substituted allylanions.

EXPERIMENTAL

IR: Perkin-Elmer PE 298. - ^1H NMR: Bruker WM-300 (300 MHz), internal reference tetramethylsilane. - ^{13}C NMR: Bruker WM-300 (75.47 MHz) and AM-360 (90.56 MHz), internal reference tetramethylsilane. - MS: Finnigan MAT C 312. - GC/MS: Varian MAT CH7A with GC Varian 1400 and data system SS200; Finnigan MAT 8230 with Varian 3400 and data system SS300. Silica capillary column OV 225 (30m).- CHN: Perkin Elmer CHN-Analysator 240.- HPLC: LiChrosorb Si60 (5 μm or 7 μm , resp., length 250 mm, diameter 16mm).- Flash chromatography: Kieselgel 60 (Merck), 0.040-0.063 mm.- Melting points are uncorrected. - All solvents are rigorously dried by standard methods. All experiments are carried out with complete exclusion of moisture (argon; septum - syringe technique) in glass ware, which is thoroughly dried by repeated heating under argon and subsequent evacuation.

2,2-Diethyl-N-phenylacetimidoyl chloride: 11.49 g (0.06 mol) of 2-ethyl-(*N*-phenyl)-butyramide are dissolved in toluene (150 ml) and treated with 12.51 g (0.06 mol) of PCl_5 . After heating to 80°C for 4 h, the mixture is stirred at room temp. for 2d more (see also ²⁰). Distillation in vacuo yields 11.69 g (93%) of the imidoyl chloride (b.p. 60°C/0.3 mbar).- IR (neat): $\bar{\nu} = 3070\text{ cm}^{-1}$ (w, CH_{aryl}), 3040 (w, CH_{aryl}), 3020 (w, CH_{aryl}), 2950 (vs, $\text{CH}_{\text{aliph.}}$), 2920 (s, $\text{CH}_{\text{aliph.}}$), 2880 (m, sh, $\text{CH}_{\text{aliph.}}$), 2860 (s, $\text{CH}_{\text{aliph.}}$), 1680 (vs, br, C=N), 1590 (s, C=C $_{\text{aryl}}$), 1575 (m, C=C $_{\text{aryl}}$), 1480 (s, C=C $_{\text{aryl}}$), 1450 (s), 1440 (s, sh), 1380 (m), 1335 (w), 1250 (w), 1215 (w), 1205 (w), 1150 (m), 1130 (s), 1065 (s), 1035 (w), 1020 (w), 1000 (w). - ^1H NMR (CDCl_3): $\delta = 1.05$ [t, $^3J = 7.15\text{ Hz}$, 6H, 2 (CH_3CH_2)], 1.70 [m, 2H, 2 (CH_3CHH)], 1.80 [m, 2H, 2 (CH_3CHH)], 2.65 (m, 1H, CHCN), 6.49 (m, 2H, CH_{meta}), 7.20 (m, 1H, CH_{para}), 7.36 (m, 2H, CH_{ortho}). - ^{13}C NMR (CDCl_3): $\delta = 11.81$ [$(\text{CH}_3\text{-CH}_2)_2$], 25.97 [$(\text{CH}_3\text{-CH}_2)_2$], 55.54 [$\text{CH}(\text{CH}_2\text{-CH}_3)_2$], 120.4 (CH_{ortho}), 125.1 (CH_{para}), 129.0 (CH_{meta}), 147.5 (C_{ipso}), 151.4 (CCIN). - MS (70eV), m/z (%): 209 (22) [M^+], 174 (48) [$\text{M}^+\text{-Cl}$], 173 (72) [$\text{M}^+\text{-HCl}$], 158 (100) [173-HCl], 144 (26), 104 (89), 93 (78), 77 (100) [C_6H_5^+]. - $\text{C}_{12}\text{H}_{16}\text{NCl}$ (209.62): calcd. C, 68.76; H, 7.69; N, 6.68; found C, 68.38; H, 7.75; N, 6.43.

N-Phenyl-diethylketenimine (1): To a solution of 10.30 g (0.06 mol) of 2,2-diethyl-*N*-phenyl-acetimidoyl chloride in toluene (180 ml) 40.6 ml (0.29 mol) of triethylamine are added. After heating for 19 h at 70°C, the reaction mixture is stirred for 72 h at room temp. The precipitated ammonium salt is filtered off and washed several times with toluene. Distillation of the combined toluene solution yields 5.77 g (55%) of ketenimine **1**. (b.p. 60-64°C/0.04 mbar). The yield of triethylamine hydrochloride amounts to 95% (0.05 mol, 6.85g).- IR (neat): $\bar{\nu} = 3040\text{ cm}^{-1}$ (w, CH_{aryl}), 3020 (w, CH_{aryl}), 2950 (s, $\text{CH}_{\text{aliph.}}$), 2920 ($\text{CH}_{\text{aliph.}}$), 2860 (m, $\text{CH}_{\text{aliph.}}$), 2840 (m, $\text{CH}_{\text{aliph.}}$), 2000 (vs, C=C=N), 1585 (s, CH_{aryl}), 1575 (m, sh, CH_{aryl}), 1480 (vs, CH_{aryl}), 1450 (m), 1390 (m), 1370 (m), 1320 (m), 1300 (m), 1280 (w), 1180 (w), 1150 (w), 1065 (m), 1020 (w). - ^1H NMR (CDCl_3): $\delta = 1.20$ [t, $^3J = 7.39\text{ Hz}$, 6H, (CH_3CH_2)₂], 2.18 [q, $^3J = 7.39\text{ Hz}$, 4H, (CH_3CH_2)₂], 7.21-7.29 (m, 1H, CH_{para}), 7.30-7.35 (m, 2H, CH_{ortho}), 7.35-7.43 (m, 2H, CH_{meta}). - ^{13}C NMR (CDCl_3): $\delta = 12.91$ [$(\text{CH}_3\text{CH}_2)_2$], 22.54 [$(\text{CH}_3\text{CH}_2)_2$], 73.60 (C=C=N), 123.8 (CH_{ortho}), 126.8 (CH_{para}), 129.3 (CH_{meta}), 144.4 (C_{ipso}), 195.9 (C=C=N). - MS (70eV), m/z (%): 173 (42) [M^+],

158 (100) [M⁺-CH₃], 144 (10) [M⁺-CH₃CH₂], 104 (80) [Ph-N=CH⁺], 77 (80) [Ph⁺]. - C₁₂H₁₅N (173.26): calcd. C, 83.19; H, 8.73; N, 8.08; found C, 83.16; H, 8.62; N, 7.70.

General procedure for the deprotonation of N-phenyl-diethylketenimine (1): A 50 ml Schlenk flask, equipped with septum and argon inlet, is filled with 0.900 g (8.0 mmol) KOtBu and *tert*.butylmethyl ether (20 ml) by use of a syringe. The mixture is cooled to -30°C, then 1.35 ml (8.0 mmol) of 2,2,6,6-tetramethylpiperidine is added. The suspension is cooled to -100°C and treated dropwise with 5.00 ml (8.0 mmol) of *n*-butyllithium (1.6 M solution in *n*-hexane). Within 25 min the mixture is allowed to warm to -78°C. Now, 0.693 g (4.0 mmol) of *N*-phenyl-diethylketenimine (**1**), dissolved in *tert*.butylmethyl ether (10 ml), is added dropwise; after 5 min the suspension turns orange and later it becomes deep red. After complete addition the suspension is allowed to warm to -20°C within 2.5 h; this temperature is maintained for 1 h; afterwards, the suspension of the *organometallic intermediates* is cooled again to -78°C.

General procedure for the aqueous work up of the crude products after the trapping reaction:

The crude reaction mixture is poured into a solution of diethyl ether (50 ml) and petroleum ether (200 ml); this mixture is washed with two portions of 30 ml of water. The combined organic layers are dried over MgSO₄, and the solvent is removed *in vacuo*.

Trapping of the organometallic intermediates with trimethylacetyl chloride: 1-(2,2-Dimethyl-1-oxo-propyl)-bis-2,4-(diethylmethylene)-3-phenyl-1,2,3,4-tetrahydroquinazoline (2), 2-(1,1-Diethyl-2-oxo-3,3-dimethyl-butyl)-3-phenyl-4-(1-ethylpropylidene)-3,4-dihydroquinazoline (3) and 2-(1,1-Diethyl-2-oxo-3,3-dimethyl-butyl)-3-phenyl-4-(1-ethylpropenylidene)-3,4-dihydroquinazoline (4): The cold suspension of the organometallic intermediates is treated dropwise with 2.03 g (16.8 mmol) of trimethylacetyl chloride within 5 min by use of a syringe. After warming to room temperature within 8 h., the color has become a little paler. After aqueous work up, flash chromatography (petroleum ether / diethyl ether, 100:1) of the crude product yields as a first fraction 160 mg of a mixture of **3** and **4**; the second fraction consists of solid **2** [R_f (DC) = 0.1], which is recrystallized from *n*-hexane. (120 mg, 14%); m.p. 100°C. The first fraction (**3** and **4**) is separated by HPLC (petroleum ether/diethyl ether, 100 : 1; flow: 4ml/min). One obtains 40 mg (5%) of colorless **4** (t_r value = 34.0 - 36.5 min) and 60 mg (7%) of colorless **3** (t_r value = 38.0 - 44.0 min).

1-(2,2-Dimethyl-1-oxo-propyl)-bis-2,4-(diethylmethylene)-3-phenyl-1,2,3,4-tetrahydro-quinazoline(2): IR(KBr): $\tilde{\nu}$ = 3080 cm⁻¹ (w, CH_{aryl}), 3060 (w, CH_{aryl}), 3020 (w, CH_{aryl}), 2960 (vs, CH_{aliph.}), 2920 (s, CH_{aliph.}), 2895 (m, sh, CH_{aliph.}), 2860 (s, CH_{aliph.}), 1710 (m), 1680 (s, NC=O), 1650 (m, br, C=C_{olef.}), 1590 (m, C=C_{aryl}), 1550 (m, C=C_{aryl}), 1485 (s, C=C_{aryl}), 1470 (m), 1450 (m), 1430 (w), 1390 (m), 1370 (m), 1360(m), 1300 (m, sh), 1280 (m), 1220 (m), 1165 (m, sh), 1150 (w), 1110 (w), 1100 (w, sh), 1070 (w), 1030 (w), 1000 (w). - ¹H NMR (CDCl₃): δ = 0.88 (t, ³J = 7.54 Hz, 3H, CH₃CH₂), 1.00 [t, ³J = 7.54 Hz, 6H, 2 (CH₃CH₂)], 1.02 [s, 9H, (CH₃)₃C], 1.15 (t,

$^3J = 7.54$ Hz, 3H, CH_3CH_2), 1.87 (q, $^3J = 7.54$ Hz, 2H, CH_3CH_2), 2.21 (q, $^3J = 7.54$ Hz, 2H, CH_3CH_2), 2.30 (q, $^3J = 7.54$ Hz, 2H, CH_3CH_2), 2.42 (q, $^3J = 7.54$ Hz, 2H, CH_3CH_2), 7.00-7.22 (m, 5H, CH_{aryl}), 7.45 (m, 1H, CH_{aryl}), 7.80 (tt, $^3J = 7.36$ Hz, $^4J = 1.14$ Hz, 1H, CH_{para}), 7.85 (m, 2H, CH_{aryl}). - ^{13}C NMR (CDCl_3): $\delta = 11.59$ (CH_3CH_2), 12.16 (CH_3CH_2), 12.49 (CH_3CH_2), 13.37 (CH_3CH_2), 22.98 (CH_3CH_2), 23.56 (CH_3CH_2), 23.62 (CH_3CH_2), 23.92 (CH_3CH_2), 28.98 [$(\text{CH}_3)_3\text{C}$], 41.75 [$(\text{CH}_3)_3\text{C}$], 120.5 (CH_{aryl}), 121.4 (CH_{aryl}), 123.4 (C=C-N), 125.8 (CH_{aryl}), 126.0 (CH_{aryl}), 126.4 (CH_{aryl}), 126.7 (CH_{aryl}), 128.5 (CH_{aryl}), 132.1 (C=C-N), 132.8 (C=CN₂), 137.3 (C_{ipso}), 140.3 (C_{ipso}), 140.5 (C=CN₂), 147.6 (C_{ipso}), 177.2 (NC=O). - MS (GC-MS), m/z (%): 430 (7) [M^+], 415 (6) [$\text{M}^+ - \text{CH}_3$], 400 (6) [415- CH_3], 373 (22) [$\text{M}^+ - \text{C}_4\text{H}_9$], 345 (65) [$\text{M}^+ - \text{C}_5\text{H}_9\text{O}$], 331 (12), 301 (12), 172 (8), 104 (8), 77 (14) [C_6H_5^+], 57 (100) [C_4H_9^+], 41 (41). - $\text{C}_{29}\text{H}_{38}\text{N}_2\text{O}$ (430.63): calcd. C, 80.89; H, 8.89; N, 6.51; found C, 80.86; H, 9.07; N, 6.55.

*X ray diffraction analysis of 2.*²¹ A light yellow, irregular crystal $\text{C}_{29}\text{H}_{38}\text{N}_2\text{O}$ (from *n*-hexane), crystal size 0.8 x 0.5 x 0.35 mm³, was measured at room temperature by using an automatic CAD4 Diffractometer (Enraf-Nonius) with Mo- K_α radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. 5577 reflexions were collected in the range $2.40 << 2\theta << 26.31^\circ$ (scan speed variable 2.75 to 16.5°/min). Crystal system: Monoclinic, space group C2/c, $Z = 8$, $a = 18.911(2)$ Å, $b = 16.963(2)$ Å, $c = 18.609(1)$ Å, $\beta = 117.29(1)^\circ$; $V = 5305.1(9)$ Å³; $D_x = 1.078$ g·cm⁻³; $\mu = 0.65$ cm⁻¹, no absorption correction. The structure was solved by direct methods (SHELXS-86 program²²) using 5375 independent reflexions. After the addition of the hydrogen atoms (coupled with respect to position and temperature parameters to the corresponding carbon atoms) anisotropic refinement led to agreement factors $R = 0.051$ and $wR2 = 0.124$ (2732 reflections with $I_0 > 2.0\sigma(I_0)$), 296 variable parameters, program SHELXL-93²³). The molecular shape is presented in Fig. 1.

2-(1,1-Diethyl-2-oxo-3,3-dimethyl-butyl)-3-phenyl-4-(1-ethylpropylidene)-3,4-dihydroquinazoline (3): IR (neat): $\bar{\nu} = 3075$ cm⁻¹ (m, CH_{aryl}), 3050 (m, CH_{aryl}), 3020 (m, sh, CH_{aryl}), 2985 (s, sh, CH_{aliph}), 2935 (s, CH_{aliph}), 2910 (s, CH_{aliph}), 2860 (s, CH_{aliph}), 1685 (vs, C=O), 1675 (s, sh, C=N), 1650 (m, C=C_{olef.}), 1600 (m, C=C_{aryl}), 1585 (m, C=C_{aryl}), 1565 (s, C=C_{aryl}), 1545 (s), 1485 (s, C=C_{aryl}), 1475 (s), 1460 (s), 1450 (s), 1405 (w), 1375 (m), 1355 (m), 1345 (m), 1310 (m, sh), 1300 (m), 1265 (s, sh), 1255 (s), 1210 (s), 1150 (m), 1130 (m), 1070 (w), 1060 (s), 1045 (s), 1030 (s), 1000 (s). - ^1H NMR (D_3CNO_2 , 353K): 0.77 [t, $^3J = 7.35$ Hz, 6H, 2 (CH_3CH_2)], 1.04 (t, $^3J = 7.54$ Hz, 3H, CH_3CH_2), 1.07 (t, $^3J = 7.43$ Hz, 3H, CH_3CH_2), 1.23 [s, 9H, $(\text{CH}_3)_3\text{C}$], 1.95 (m, 2H, CH_3CH_2), 2.22 (m, 2H, CH_3CH_2), 2.52 (q, $^3J = 7.48$ Hz, 1H, CH_3CH_2), 2.85 (q, $^3J = 7.53$ Hz, 1H, CH_3CH_2), 7.10-7.45 (m, 9H, CH_{aryl}). - ^{13}C NMR (CDCl_3): $\delta = 8.09$ [2 (CH_3CH_2)], 9.45 (CH_3CH_2), 10.97 (CH_3CH_2), 19.90 (CH_3CH_2), 20.06 (CH_3CH_2), 27.11 (CH_3CH_2), 27.39 [$(\text{CH}_3)_3\text{C}$], 27.61 (CH_3CH_2), 43.89 [$(\text{CH}_3)_3\text{C}$], 63.07 (C-CN₂), 122.1 (CH_{aryl}), 124.0 (CH_{aryl}), 124.7 (CH_{aryl}), 125.4 (CH_{aryl}), 126.2 (CH_{aryl}), 126.9 (CH_{aryl}), 127.1 (CH_{aryl}), 129.5 (C=C-N), 138.0 (C=C-N), 141.3 (C_{ipso}), 142.8 (C_{ipso}), 161.0 (C=N), 211.3 (C=O). MS (70 eV), m/z (%): 430 (12) [M^+], 415 (10) [$\text{M}^+ - \text{CH}_3$], 373 (14) [$\text{M}^+ - \text{C}_4\text{H}_9$], 345 (30) [$\text{M}^+ - \text{C}_5\text{H}_9\text{O}$], 329 (16), 315 (15), 301 (16), 85 (24) [$\text{C}_5\text{H}_9\text{O}^+$], 57 (100) [C_4H_9^+].

2-(1,1-Diethyl-2-oxo-3,3-dimethyl-butyl)-3-phenyl-4-(1-ethylpropenylidene)-3,4-dihydroquinazoline(4): IR (neat): $\bar{\nu}$

= 3080 cm^{-1} (m, CH_{aryl}), 3060 (m, CH_{aryl}), 3020 (m, sh, CH_{aryl}), 2985 (s, sh, CH_{aliph}), 2935 (s, CH_{aliph}), 2910 (s, CH_{aliph}), 2860 (s, CH_{aliph}), 1685 (vs, C=O), 1675 (s, sh, C=N), 1650 (w, C=C_{olef}), 1605 (m, C=C_{aryl}), 1590 (m, C=C_{aryl}), 1565 (s, C=C_{aryl}), 1555 (s, sh), 1545 (s), 1485 (s, C=C_{aryl}), 1475 (s), 1460 (s), 1445 (s), 1405 (w), 1385 (m), 1370 (w), 1355 (m), 1350 (m), 1345 (m), 1310 (m, sh), 1300 (m), 1280 (m, sh), 1265 (s, sh), 1255 (s), 1210 (s), 1180 (m), 1170 (m), 1150 (m), 1130 (m), 1110 (m), 1090 (w), 1070 (w), 1060 (s), 1045 (s), 1030 (s), 1000 (s). - ^1H NMR (CDCl_3): δ = 0.68 (t, 3J = 7.16 Hz, 3H, CH_3CH_2), 0.79 (m, 3H, CH_3CH_2), 1.02 [s, 9H, $(\text{CH}_3)_3\text{C}$], 1.04 (t, 3J = 7.51 Hz, 3H, CH_3CH_2), 1.70 (s, br, 2H, CH_3CH_2), 2.05 (s, br, 2H, CH_3CH_2), 2.47 (q, 3J = 7.16 Hz, 2H, CH_3CH_2), 5.26 (dd, 2J = 1.13 Hz, 3J = 10.92 Hz, 1H, $\text{HHC}=\text{CH}$), 5.37 (dd, 2J = 1.13 Hz, 3J = 17.71 Hz, 1H, $\text{HHC}=\text{C}$), 6.93-7.23 (m, 7H, CH_{aryl}), 7.24- 7.29 (m, 2H, CH_{aryl}), 7.42 (dd, 3J = 10.93 Hz, 3J = 17.71 Hz, 1H, $\text{HHC}=\text{CH}$). - ^1H NMR (D_3CNO_2 , 353K): 0.80 [t, 3J = 7.39 Hz, 6H, 2 (CH_3CH_2)], 1.14 (t, 3J = 7.39 Hz, 3H, CH_3CH_2), 1.19 [s, 9H, $(\text{CH}_3)_3\text{C}$], 1.90 (q, 3J = 7.39 Hz, 1H, CH_3CHH), 1.92 (m, 3J = 7.39 Hz, 1H, CH_3CHH), 2.18 (m, 3J = 7.39 Hz, 1H, CH_3CHH), 2.20 (q, 3J = 7.39 Hz, 1H, CH_3CHH), 2.66 (q, 3J = 7.39 Hz, 2H, CH_3CH_2), 5.46 (dd, 2J = 1.13 Hz, 3J = 10.92 Hz, 1H, $\text{HHC}=\text{CH}$), 5.57 (dd, 2J = 1.13 Hz, 3J = 17.71 Hz, 1H, $\text{HHC}=\text{C}$), 7.08-7.50 (m, 9H, CH_{aryl}), 7.68 (dd, 3J = 10.93 Hz, 3J = 17.71 Hz, 1H, $\text{HHC}=\text{CH}$). - ^{13}C NMR (CDCl_3): δ = 9.08 [2 (CH_3CH_2)], 14.61 (CH_3CH_2), 20.10 (CH_3CH_2), 27.32 [2 (CH_3CH_2)], 29.61[(CH_3)₃C], 45.77 [(CH_3)₃C], 65.07 (C-CN₂), 114.9 ($\text{H}_2\text{C}=\text{CH}$), 124.5 (CH_{aryl}), 125.5 (C_{ipso}), 126.4 (CH_{aryl}), 126.7 (CH_{aryl}), 128.4 (CH_{aryl}), 128.9 (CH_{aryl}), 133.8 ($\text{H}_2\text{C}=\text{CH}$), 135.0 (C=C-N), 136.3 (C=CN), 142.8 (C_{ipso}), 144.9 (C_{ipso}), 162.5 (C=N), 212.4 (C=O). - ^{13}C NMR (D_3CNO_2 , 353 K): δ = 10.02 [2 (CH_3CH_2)], 15.01 (CH_3CH_2), 22.20 (CH_3CH_2), 29.25[(CH_3)₃C], 31.20 [2 (CH_3CH_2)], 48.87 [(CH_3)₃C], 67.10 (C-CN₂), 114.9 ($\text{H}_2\text{C}=\text{CH}$), 125.0 (CH_{aryl}), 126.1 (C_{ipso}), 126.5 (CH_{aryl}), 126.9 (CH_{aryl}), 128.4 (CH_{aryl}), 129.1 (CH_{aryl}), 134.2 ($\text{H}_2\text{C}=\text{CH}$), 135.9 (C=C-N), 139.3 (C=CN), 143.8 (C_{ipso}), 146.7 (C_{ipso}), 164.5 (C=N), 214.4 (C=O). - MS (70 eV), m/z (%): 428 (15) [M^+], 413 (12) [M^+-CH_3], 399 (12) [$\text{M}^+-\text{C}_2\text{H}_5$], 371 (12) [$\text{M}^+-\text{C}_4\text{H}_9$], 343 (44) [$\text{M}^+-\text{C}_5\text{H}_9\text{O}$], 330 (14), 315 (14), 299 (16), 85 (24) [$\text{C}_5\text{H}_9\text{O}^+$], 57 (100) [C_4H_9^+]. - $\text{C}_{26}\text{H}_{36}\text{N}_2\text{O}$ calcd. 428.2827; found 428.2812 (MS).

Trapping of the organometallic intermediates with dimethyl disulfide: 4-Diethylmethylene-2-(1-ethyl-1-thiomethyl-propyl)-3-phenyl-3,4-dihydroquinazoline (5), 2-(1-Ethyl-1-thiomethyl-propyl)-4-(Z-1-ethyl-2-thiomethylpropylidene)-3-phenyl-3,4-dihydroquinazoline (6) and 2-(1-Ethyl-1-thiomethyl-propyl)-4-(E-1-ethyl-2-thiomethyl-propylidene)-3-phenyl-3,4-dihydro-quinazoline (7): After addition of 1.51 ml (16.8 mmol) of dimethyl disulfide to the cold (-78°C) suspension, the deep red color turns to yellow-orange. The reaction mixture is allowed to warm to room temperature over night; then aqueous work up follows. Flash chromatography (petroleum ether / diethyl ether, 200:1) yields two fractions. The first fraction (R_f (DC) = 0.20) is separated by HPLC; one obtains 165 mg (21%) **5** as light yellow crystals; m.p. 71°C (n-hexane). The second fraction (R_f (DC) = 0.14) furnishes 218 mg (29%) of a 2:1 mixture of **6** and **7**, which could not be separated further.

4-Diethylmethylene-2-(1-ethyl-1-thiomethyl-propyl)-3-phenyl-3,4-dihydroquinazoline (5): IR (KBr): $\tilde{\nu}$ = 3070 cm^{-1} (w, CH_{aryl}), 3060 (w, CH_{aryl}), 3020 (w, CH_{aryl}), 2960 (vs, CH_{aliph}), 2930 (s, CH_{aliph}), 2870 (m, CH_{aliph}),

2830 (w, CH_{aliph.}), 1595 (m, C=C_{aryl}), 1570 (s, C=C_{olef.}), 1550 (s, C=N), 1540 (w, sh, C=C_{aryl}), 1485 (s, C=C_{aryl}), 1465 (s), 1450 (s), 1435 (m, sh), 1415 (w, sh), 1370 (w), 1345 (m), 1315 (w), 1290 (w), 1285 (w, sh), 1245 (s), 1230 (s), 1220 (s), 1195 (w, sh), 1170 (w), 1150 (w), 1135 (m), 1120 (w), 1095 (w), 1075 (w), 1050 (w), 1030 (w). - ¹H NMR (CDCl₃): δ = 0.80 (t, ³J = 7.16 Hz, 3H, CH₃CH₂), 0.92 (t, ³J = 7.35, 3H, CH₃CH₂), 1.03 (t, ³J = 7.53 Hz, 3H, CH₃CH₂), 1.05 (t, ³J = 7.53 Hz, 3H, CH₃CH₂), 1.70 (m, 1H, CH₃CHH), 1.76 (q, 1H, CH₃CHH), 1.86 (s, 3H, SCH₃), 2.35 (m, 1H, CH₃CHH), 2.41 (m, 1H, CH₃CHH), 2.57 (m, 1H, CH₃CHH), 3.01 (m, 1H, CH₃CHH), 6.79- 7.36 (m, 9H, CH_{aryl}). - ¹³C NMR (CDCl₃): δ = 8.39 (CH₃CH₂), 8.98 (CH₃CH₂), 11.63 (SCH₃), 11.80 (CH₃CH₂), 13.27 (CH₃CH₂), 21.24 (CH₃CH₂), 22.46 (CH₃CH₂), 25.61 (CH₃CH₂), 25.82 (CH₃CH₂), 58.20 (C_q-S), 122.9 (CH_{aryl}), 123.6 (CH_{aryl}), 124.6 (CH_{aryl}), 125.7 (CH_{aryl}), 126.2 (CH_{aryl}), 126.2 (C=C-N), 127.5 (CH_{aryl}), 128.6 (CH_{aryl}), 130.8 (C=C-N), 142.7 (C_{ipso}-C=C), 144.4 (C_{ipso}-N=C), 146.0 (C_{ipso}-N), 164.2 (C=N). - MS (70 eV), m/z (%): 392 (18) [M⁺], 363 (36) [M⁺-C₂H₅], 346 (100) [M⁺-CH₂S], 345 (80) [M⁺-CH₃S], 331 (93) [345-CH₃], 317 (76) [346-C₂H₅], 315 (80) [M⁺-C₆H₅], 301 (64), 287 (60), 271 (42), 257 (26), 250 (24), 172 (58), 158 (50), 117 (86), 91 (56) [C₇H₇⁺], 77 (82) [C₆H₅⁺]. - C₂₅H₃₂N₂S (392.60): calcd. C, 76.48; H, 8.22; N, 7.13; found C, 76.61; H, 8.28; N, 7.23.

*X ray diffraction analysis of 5:*²¹ A colorless, needle shaped crystal C₂₅H₂₃N₂S (from *n*-hexane), crystal size 0.5 x 0.15 x 0.1 mm³, was measured at room temperature by using an automatic CAD4 Diffractometer (Enraf-Nonius) with Cu-K_α radiation (λ = 1.54178 Å) and a graphite monochromator. 4329 reflexions were collected in the range 3.93 << 2θ << 74.24° (scan speed variable 4.13 to 16.5°/min). Crystal system: Triclinic, space group P₁[̄], Z = 2, a = 9.431(1) Å, b = 10.625(1) Å, c = 11.266(1) Å, α = 88.01(1), β = 88.20(1), γ = 86.71(1)°; V = 1125.2(2) Å³; Dx = 1.159 g·cm⁻³; μ = 13.5 cm⁻¹, no absorption correction. The structure was solved by direct methods (SHELXS-86 program²²) using 4102 independent reflexions. After the addition of the hydrogen atoms (coupled with respect to position and temperature parameters to the corresponding carbon atoms) anisotropic refinement led to agreement factors R = 0.051 and wR2 = 0.130 (2666 reflections with I_o > 2.0σ(I_o), 258 variable parameters, program SHELXL-93²³). The molecular shape is presented in Fig. 2.

2-(1-Ethyl-1-thiomethyl-propyl)-4-(Z-1-ethyl-2-thiomethylpropylidene)-3-phenyl-3,4-dihydroquinazoline (6) and 2-(1-Ethyl-1-thiomethyl-propyl)-4-(E-1-ethyl-2-thiomethyl-propylidene)-3-phenyl-3,4-dihydroquinazoline (7): IR (KBr): ν̄ = 3070 cm⁻¹ (w, CH_{aryl}), 3060 (w, CH_{aryl}), 3030 (w, CH_{aryl}), 2965 (vs, CH_{aliph.}), 2930 (m, CH_{aliph.}), 2920 (m, sh, CH_{aliph.}), 2870 (m, CH_{aliph.}), 2830 (w, CH_{aliph.}), 1595 (m, C=C_{aryl}), 1570 (m, C=C_{olef.}), 1550 (s, C=N), 1540 (w, sh, C=C_{aryl}), 1490 (m, C=C_{aryl}), 1465 (m), 1450 (s), 1425 (w, sh), 1380 (w), 1370 (w, sh), 1315 (w), 1295 (w), 1260 (w, sh), 1240 (m), 1215 (m), 1155 (w), 1135 (m), 1120 (m), 1095 (w), 1075 (w), 1050 (w), 1030 (w). - ¹H NMR (CDCl₃): δ = 0.69 (t, ³J = 7.26 Hz, 3H, CH₃CH₂), 0.74 - 1.10 (m, 15H, CH₃CH₂), 1.38 (d, ³J = 6.40 Hz, 6H, CH₃CH), 1.63 (m, 4H, CH₃CH₂), 1.82 (s, 3H, SCH₃), 1.84 (s, 3H, SCH₃), 1.95 (s, 3H, SCH₃), 2.10 (m, 4H, CH₃CH₂), 2.14 (s, 3H, SCH₃), 2.41 (m, 4H, CH₃CH₂), 4.91 (q, ³J = 6.78 Hz, 1H, CH₃CHS), 5.18 (q, ³J = 6.44 Hz, 1H, CH₃CHS), 6.84- 7.37 (m, 18H, CH_{aryl}). - ¹³C NMR (CDCl₃): δ = 8.26 (CH₃CH₂), 8.59 (CH₃CH₂), 8.93 (CH₃CH₂), 9.00 (CH₃CH₂), 11.49 (SCH₃), 11.59 (SCH₃), 14.39 (SCH₃), 15.00 (CH₃CH₂), 15.50

(SCH₃), 15.90 (CH₃CH₂), 19.68 (CH₃CH, CH₃CH₂), 19.98 (CH₃CH, CH₃CH₂), 25.00 (CH₃CH₂), 25.58 (CH₃CH₂), 26.15 (CH₃CH₂), 27.33 (CH₃CH₂), 41.48 (CH₃CH), 42.76 (CH₃CH), 57.83 (C_q-S), 58.10 (C_q-S), 122.8 (CH_{aryl}), 124.0 (CH_{aryl}), 124.7 (CH_{aryl}), 125.6 (CH_{aryl}), 125.7 (C_q), 125.8 (C_q), 125.9 (CH_{aryl}), 126.1 (CH_{aryl}), 126.3 (CH_{aryl}), 126.8 (CH_{aryl}), 127.9 (CH_{aryl}), 128.0 (CH_{aryl}), 128.6 (CH_{aryl}), 133.5 (C_q), 134.2 (C_q), 140.4 (C_q), 142.3 (C_q), 143.0 (C_q), 143.7 (C_q), 145.7 (C_q), 145.8 (C_q), 163.7 (C=N), 163.8 (C=N). MS (DCI-NH₃), m/z (%): 439 (39) [M⁺+1], 391 (18) [M⁺-SCH₃], 345 (100) [391-SCH₂]. - C₂₆H₃₄N₂S₂ + H: calcd. 439.2242; found 439.2188 (MS, DCI-NH₃).

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We dedicate this paper to *Prof. Dr. M. Regitz* at the occasion of his 60th birthday.

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