Tandem Hydroformylation/Reductive Amination of 3-Allyl-2-methylquinazolin-4(3*H*)-one

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The 3-allyl-2-methylquinazolin-4(3*H*)-one (**1**), a model functionalized terminal olefin, was submitted to hydroformylation and reductive amination under optimized reaction conditions. The catalytic carbonylation of **1** in the presence of Rh catalysts complexed with phosphorus ligands under different reaction conditions afforded a mixture of 2-methyl-4-oxoquinazoline-3(4*H*)-butanal (**2**) and α,2-dimethyl-4-oxoquinazoline-3(4*H*)-propanal (**3**) as products of 'linear' and 'branched' hydroformylation, respectively (*Scheme 2*). The hydroaminomethylation of quinazolinone **1** with arylhydrazine derivatives gave the expected mixture of [(arylhydrazinyl)alkyl]quinazolinones **5** and **6**, besides a small amount of **2** and **3** (*Scheme 3*). The tandem hydroformylation/reductive amination reaction of **1** with different amines gave the quinazolinone derivatives **7**–**10**. Compound **10** was used to prepare the chalcones **11a** and **11b** and pyrazoloquinazolinones **12a** and **12b** (*Scheme 4*).

Introduction. – Diverse biological activity is encountered in organic compounds containing the quinazoline system, especially the 2,3-disubstituted quinazolin-4(3*H*)-one derivatives possess a broad spectrum of biological and pharmaceutical activities [1–7]. From a synthetic chemist's point of view, synthetic strategies that give a convenient and fast access to highly functionalized diverse libraries of quinazolin-4(3*H*)-one derivatives are in demand.

'Hydroformylation of terminal olefins is established as an important industrial tool for the production of aldehydes and products derived therefrom. This process starts from petrochemicals (alkenes) and various other basic feed stocks (CO, H_2). As a straightforward addition reaction of inexpensive starting materials, it is a clean and economical method' [8]. On the other hand, tandem reaction sequences are of great interest; they enabled the atom-economic formation of C–C bonds, thus providing relatively easy access to complex molecular architectures [9].

The present work is an extension of our ongoing efforts towards the synthesis of new interesting 2,3-disubstituted quinazoline derivatives in a modern fashion (*via* hydroformylation and reductive amination), which are a source of functionalized molecules possessing many biological applications.

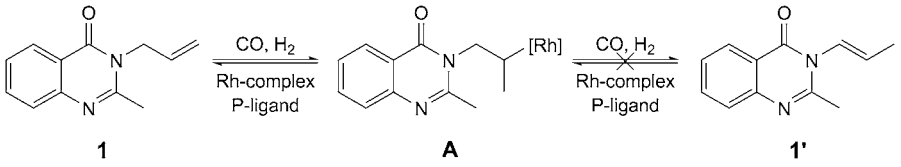
Results and Discussion. – In the present study, 3-allyl-2-methylquinazolin-4(3*H*)-one (=2-methyl-3-(prop-2-en-1-yl)quinazolin-4(3*H*)-one; **1**) [10] was chosen as a

model for a functionalized terminal olefin. It was obtained by the reaction of 2-methylquinazolin-4(3*H*)-one with allyl bromide in the presence of NaH in THF/DMF.

Despite the variety of preparative approaches to 2,3-disubstituted quinazolinone derivatives, there is so far no report on the use of a 3-allyl substituent as a possible reactive moiety for the generation of a second chromophore at the 3-position of quinazolinones. A hydroformylation has many attractive features: the reaction needs only catalytic amounts of a metal complex, it introduces the reactive aldehyde functionality, and all atoms of the starting materials remain incorporated into the product in a very economical C–C bond forming reaction [11].

Thus, **1** was submitted to catalytic carbonylation in the presence of a Rh-catalyst [(Rh(acac)(CO)$_2$] or [{Rh(cod)Cl}$_2$] (acac = acetylacetonato = pentane-2,4-dionato; cod = cycloocta-1,5-diene) [12][13] complexed *in situ* with a phosphorus ligand at moderate temperature (60–80°) under various reaction conditions (CO and H_2 gases pressure (10–40 bar), reaction time (1–4 d), and solvent (THF, AcOH, 1,4-dioxane). No conversion was observed, only hydrogenation products were obtained besides the starting material. Taking into account the generally accepted mechanism of hydroformylation [14][15], we can propose that, under these conditions, the branched alkylrhodium intermediate **A** undergoes a β-elimination process generating the olefin **1** but not **1′** (*Scheme 1*); in contrast to the behavior observed with other olefins, *e.g.*, allylbenzene [16–18].

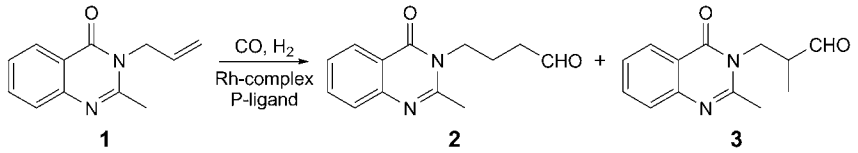
Scheme 1



In fact, no traces of the internal olefin **1′** were observed in the crude reaction mixture either after partial or after total conversion. As a consequence of the electron-withdrawing effect of the heteroaromatic residue, the H-atom bonded to the C-atom vicinal to the ring N-atom in **A** does not have enough hydridic character to take part in β-hydride elimination. This very interesting result indicates that the hydroformylation conditions are compatible with the quinazolinone-functionalized olefin employed and allow the olefin to exist even under forcing conditions that would favor isomerization (high temperature and low pressure).

These facts enforced us to apply the above-described hydroformylation reaction in the presence of [Rh(acac)(CO)$_2$] and P-ligand at more elevated temperature (100–120°) and low gas pressures (up to 20 bar for H_2 and 40 bar for CO), which yielded a mixture of 2-methyl-4-oxoquinazoline-3(4*H*)-butanal (**2**) and α,2-dimethyl-4-oxoquinazoline-3(4*H*)-propanal (**3**) as the products of 'linear' and 'branched' hydroformylation, respectively (*Scheme 2*).

Scheme 2



Temperature had a strong influence on the regioselectivity of the hydroformylation of **1**. At lower temperature (100°), the ratio **2**/**3** was 79 : 21, while at 120° the ratio was 69 : 31 (*Table 1*). Also the effect of ligand basicity on the **2**/**3** ratio was studied. When a monodentate phosphorus ligand like $(PhO)_3P$ was used, a high regioselectivity towards the unbranched aldehyde **2** was observed, in agreement with our previous results [19]. However, the use of a bidentate ligand (more basic) like biphephos (=6,6′-{[3,3′-bis-(1,1-dimethylethyl)-5,5′-dimethoxy[1,1′-biphenyl]-2,2′-diyl]bis(oxy)}bis[dibenzo[*d*,*f*]-[1,3,2-dioxaphosphepin]), resulted in a higher conversion, and the regioselectivity towards the unbranched aldehyde **2** was decreased (*Table 1*). It was reported [20][21] that the activity of less basic ligands is higher because the electron-withdrawing ligands decreased the back-donation to CO and thus weakened the binding of the carbonyl. The effect of the basicity of the monodentate ligand on the regioselectivity could be explained by the basicity of the hydride. A basic phosphine leads to an increase in the nucleophilicity of the hydride. Therefore, the interaction of the hydride with the terminal C-atom (which bears a more positive fractional charge than the C(β)-atom) is favored, leading to smaller amounts of branched aldehyde **3**. Moreover, the hydroformylation reaction was carried out with the above-mentioned stable Rh catalyst under the same reaction conditions but in the absence of excess phosphorus ligand (*Table 1*, *Entry 6*), and a 73% conversion was obtained. This can be interpreted on the basis of Rh-catalyst deactivation that is neglected in the absence of phosphorus ligands, which leads to a high conversion, but the regioselectivity is markedly decreased.

Table 1. *Synthesis of Butanal* **2** *and Propanal* **3**[a])

Entry	p(CO) [bar]	$p(H_2)$ [bar]	Temp. [°]	Time [d]	Ligand	Yield [%]	Conversion [%]	Ratio **2**/**3**
1	20	10	100	4	$(PhO)_3P$	–	–	–
2	20	10	120	4	$(PhO)_3P$	–	–	–
3	40	10	100	4	$(PhO)_3P$	68	27	79 : 21
4	40	10	120	4	$(PhO)_3P$	74	43	69 : 31
5	40	10	120	5	$(PhO)_3P$	87	55	88 : 12
6	40	10	120	5	–	92	73	62 : 38
7	40	10	120	5	biphephos	79	66	69 : 31

[a]) Conditions: 1,4-dioxane, $[Rh(acac)(CO)_2]$.

A possible criticisms of the above-described hydroformylation of quinazolinone **1** is that it provides only a C_1 chain elongation (low synthetic efficiency) and it requires control of regioselectivity. These troublesome problems can be solved in a new hydroformylation-based domino process for the generation of interesting quinazoline derivatives with an attractive side chain at the 3-position. Thus, the hydroaminome-

thylation of **1** was investigated as an atom-economical efficient one-pot synthesis of amines. If the hydroformylation of **1** was conducted in the presence of arylhydrazines **4a**–**4d**, the expected (2-arylhydrazinyl)alkyl-substituted quinazolinones **5** and **6** could be isolated in very high yields (*Scheme 3*, *Table 2*). Herein, the one-pot reaction involved the hydroformylation chosen at the optimum reaction conditions, the condensation of the formed aldehydes with arylhydrazines **4a**–**4d** to give the corresponding hydrazone derivatives, and subsequent hydrogenation to afford the desired 3-[(2-arylhydrazinyl)alkyl]quinazolin-4(3*H*)-ones **5a**–**5d** and **6a**–**6d**. *Beller* and co-workers have also found that aldehydes can be trapped as arylhydrazones under hydroformylation conditions [22]. Under the chosen conditions, electron-withdrawing as well as electron-donating substituents at the aromatic hydrazine **4** were tolerated. Even NO_2 groups were stable under the reductive conditions [23]. It is also important to mention that the use of a Rh/biphephos system granted high unbranched-product selectivity in the hydroformylation of the 3-allylquinazolinone system. In all cases, no hydrogenation products derived from the olefin or the intermediate aldehyde were observed, as the latter was immediately trapped by the hydrazine. In view of this

Scheme 3

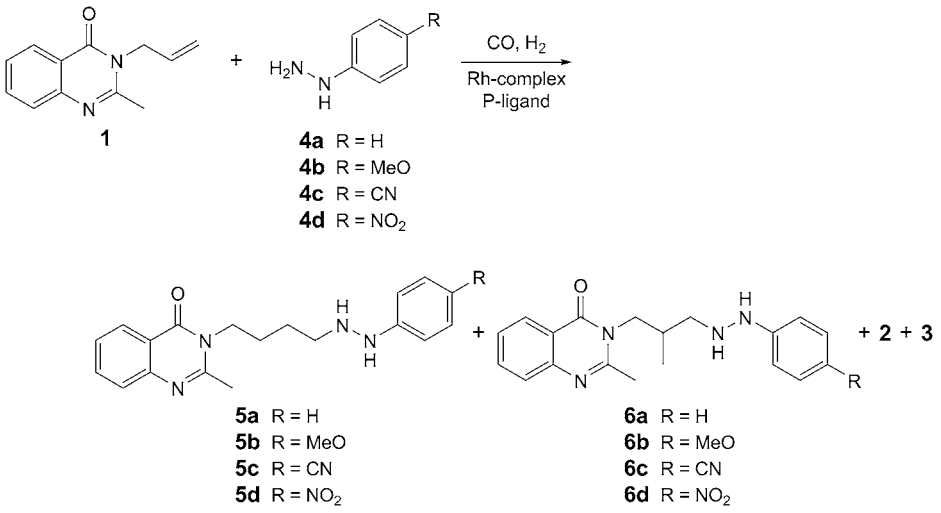


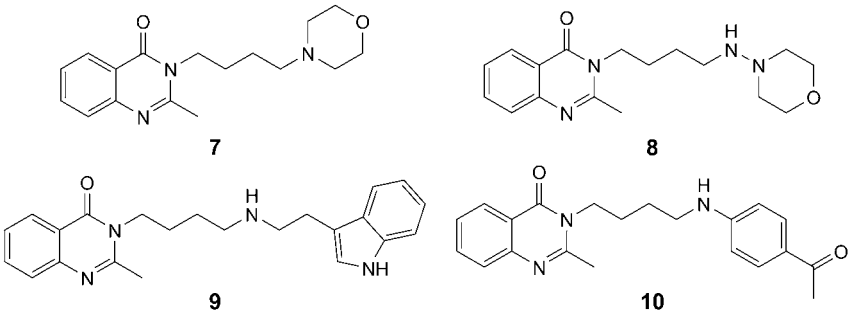
Table 2. *Tandem Hydroformylation/Hydrazone Formation*[a])

Entry	R	Yield [%]	Ratio **5**/**6**	Hydroformylation products **2**/**3** [%]
1	H	96	91 : 9	6.7
2	MeO	92	87 : 13	6.8
3	CN	89	90 : 10	6.8
4	NO_2	81	91 : 9	7.2

[a]) Conditions: 1,4-dioxane, [Rh(acac)(CO)$_2$], biphephos, $p(H_2)$ 10 bar, p(CO) 70 bar, 120°, 5 d.

trapping reaction, higher yields were achieved, and beside the hydrazinyl derivatives **5** and **6**, around 7% of the hydroformylation products **2** and **3** were found (*Table 2*). We can account for this small amount of **2** and **3** regarding the hydroformylation reaction as a reversible reaction; in our case, the aldehyde formed was trapped by the arylhydrazine and the reaction was shifted to the right.

Over the years, medicinal chemists have connected different heterocyclic rings at the 3-position of quinazolin-4(3*H*)-ones to get CNS (central nervous system) active agents and other biologically active agents [24]. We report herein on the synthesis of new 3-substituted quinazolin-4(3*H*)-ones by our modern strategy of a one-pot hydroaminomethylation reaction. Thus, the tandem hydroformylation and reductive amination reaction of **1** with different amines like morpholine, morpholin-4-amine, tryptamine, and 4-aminoacetophenone in the presence of [Rh(acac)$(CO)_2$] at 100–120° and gas pressures of 10 bar for H_2 and 60 bar for CO afforded the interesting 3-substituted quinazolinones **7**–**10**, respectively.



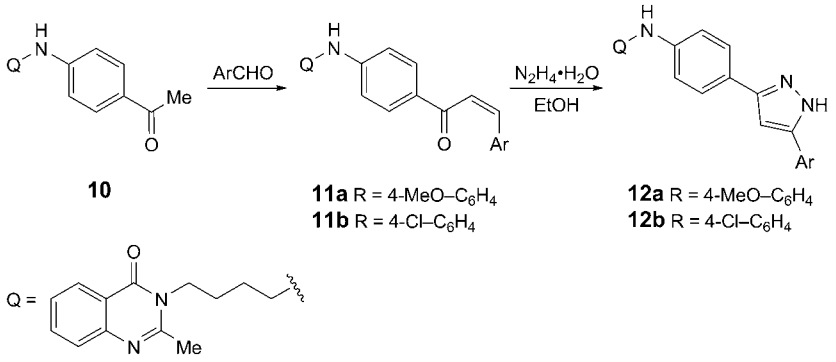
7 **8**

9 **10**

The behavior of the activated Me group in the 4-acetylphenyl moiety of quinazoline derivative **10** was investigated by its reaction with aromatic aldehydes like 4-methoxybenzaldehyde and 4-chlorobenzaldehyde, affording the corresponding chalcones **11a** and **11b** (*Scheme 4*). The reaction of such chalcones with $N_2H_4 \cdot H_2O$ is of great interest in the construction of a pharmacophore: It was established that attachment of the pyrazoline moiety to a series of quinazolin-4(3*H*)-one derivatives enhanced their biological activity [25–28]. Therefore, chalcones **11a** and **11b** were treated with $N_2H_4 \cdot H_2O$ in boiling EtOH, and the [4-(1*H*-pyrazol-3-yl)phenyl]-substituted quinazolinone derivatives **12a** and **12b** were obtained (*Scheme 4*).

Conclusion. – We successfully converted 3-allyl-2-methylquinazolin-4(3*H*)-one (**1**) into a series of new functionalized 2,3-disubstituted quinazoline derivatives. Considering the importance of 2,3-disubstituted quinazoline derivatives as biologically active compounds, the sequential hydroformylation/reductive amination reported here promises to be a useful protocol for fine chemistry.

Scheme 4



10

11a R = 4-MeO–C_6H_4
11b R = 4-Cl–C_6H_4

12a R = 4-MeO–C_6H_4
12b R = 4-Cl–C_6H_4

Experimental Part

1. *General.* All reagents and solvents were dried and purified before use by the usual procedures [29]. [Rh(acac)$(CO)_2$], PPh_3, and $P(OPh)_3$ were commercially available; biphephos and [{Rh(cod)Cl}$_2$] were prepared according to the methods described in [12][30]. Hydroformylation experiments were carried out in a *Berghof-HR-200* or in a *Parr* autoclave, high-pressure reactor with magnetic stirring and electrical heating. The inside part of the cover was made from *Teflon*® to protect the soln. from direct contact with the stainless steel. Column chromatography (CC): *MN-Kieselgel-60* (SiO_2; 0.063–0.2 mm, 70–230 mesh). TLC: *Merk* TLC aluminium sheets, silica gel *60* F_{254}; detection by UV light at 254 nm. M.p.: *Büchi*® melting-point apparatus; uncorrected. IR Spectra: FT-IR *Nicolet Impact 400D*; KBr pellets; $\tilde{\nu}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: *Bruker* instrument; at 400 and 100 MHz, resp.; in $CDCl_3$ or (D_6)DMSO; δ in ppm rel. to Me_4Si as internal standard, J in Hz; DEPT-135 spectra to assist signal assignments. HR-FAB-MS (positive-ion mode): *Jeol JMS-SX 102A*; *m/z*. Elemental analyses were carried out at the Technical University of Dortmund.

2. *2-Methyl-3-(prop-2-en-1-yl)quinazolin-4(3*H*)-one* (**1**) [10]. NaH (1.5 equiv.) in THF (5 ml) was cooled to 0° under Ar. A soln. of 2-methylquinazolin-4(3*H*)-one in THF/DMF 3:1 (20 ml) was added dropwise with stirring, then allyl bromide (1.5 equiv.) was added dropwise. The mixture was heated under reflux for 48 h. The solvent was evaporated, the residue extracted with Et_2O, the extract dried ($MgSO_4$) and concentrated, and the solid recrystallized from benzene: 0.85 g (84%) of **1**. Colorless oil. IR (KBr): 1681 (CO), 2923 (CH aliph.), 3080 (CH arom.). ^{1}H-NMR ($CDCl_3$): 2.26 (*s*, 3 H); 4.70 (*d*, J = 5.2, 2 H); 5.19 (*dd*, J = 18.1, 1.3, 2 H); 5.84–5.89 (*m*, 1 H); 7.38 (*t*, J = 7.2, 1 H); 7.56 (*d*, J = 8.0, 1 H); 7.66 (*t*, J = 8.0, 1 H); 8.19 (*d*, J = 7.2, 1 H). ^{13}C-NMR ($CDCl_3$): 14.2 (Me); 46.6 (CH_2); 117.6 (CH_2); 119.7 (C); 120.7 (C); 126.9 (CH); 127.3 (CH); 132.0 (CH); 134.7 (CH); 147.5 (CH); 154.9 (C); 162.2 (C). HR-FAB-MS (pos.): 200.2464 (M^+, $C_{12}H_{12}N_2O^+$; calc. 200.2466). Anal. calc. for $C_{12}H_{12}N_2O$ (200.24): C 71.98, H 6.04, N 13.99; found: C 72.08, H 6.11, N 13.82.

3. 3.1. *Hydroformylation: Method A.* To a soln. of [Rh(acac)$(CO)_2$] (5 mg, 0.019 mmol, 0.005 equiv.) in solvent (5 ml) in a vial was added the phosphorus ligand (0.078 mmol, 0.02 equiv.). The mixture was stirred with a magnetic stirrer for 5 min and then charged with **1** (3.8 mmol, 1 equiv.). The vial was transferred to the autoclave, pressurized, and heated. The mixture was stirred magnetically with a stirrer that mixes the gas phase and the liquid phase intensively. After the reaction was completed, the autoclave was cooled to r.t., depressurized, flushed with Ar, and opened to obtain the crude sample.

3.2. *Tandem Hydroformylation/Reductive Amination: Method B.* To a soln. of [Rh(acac)$(CO)_2$] (5 mg, 0.019 mmol, 0.005 equiv.) in 1,4-dioxane (5 ml) in a vial was added the phosphorus ligand (0.078 mmol, 0.02 equiv.). The mixture was stirred with a magnetic stirrer for 5 min and then charged with **1** (3.8 mmol, 1 equiv.) and hydrazine or amine. The reaction was then conducted as described in *Method A*. The reaction mixture was filtered through a column filled with SiO_2 and the column washed with Et_2O (50 ml). The filtrate was concentrated and the crude product purified by CC.

3.3. *2-Methyl-4-oxoquinazoline-3(4*H*)-butanal* (**2**) *and α,2-Dimethyl-4-oxoquinazoline-3(4*H*)-propanal* (**3**). *Method A* (*Table 1*, *Entry 5*), with [Rh(acac)(CO)$_2$] (5 mg, 0.019 mmol, 0.005 equiv.), P(OPh)$_3$ (24.2 mg, 0.078 mmol, 0.02 equiv.), **1** (761 mg, 3.8 mmol, 1 equiv.), 10 bar H_2, and 40 bar CO in 1,4-dioxane at 120° for 5 d. The solvent was evaporated: **2**/**3** 88 : 12 (87%), which was not further purified. Anal. data from an inseparable mixture **2**/**3**: ^{1}H-NMR ((D$_6$)DMSO): 1.13 (*d*, *J* = 6.9, 3 H); 2.17 (*quint.*, *J* = 7.3, 2 H); 2.26 (*s*, 3 H); 2.82 (*t*, *J* = 6.9, 2 H); 2.95 (*sext.*, *J* = 9.5, 1 H); 4.89 (*t*, *J* = 7.3, 2 H); 7.19–7.23 (*m*, 2 H); 7.37 (*d*, *J* = 8.0, 1 H); 7.48 (*t*, *J* = 7.7, 1 H); 9.23 (br. *s*, 1 H); 9.39 (br. *s*, 1 H). ^{13}C-NMR ((D$_6$)DMSO): major isomer: 14.3 (Me); 26.6 (CH$_2$); 34.5 (CH$_2$); 36.6 (CH$_2$); 110.3 (C); 119.6 (CH); 122.3 (CH); 124.5 (CH); 131.1 (CH); 147.8 (C); 168.2 (C); 169.4 (C); 199.6 (C); minor isomer: 12.9 (Me); 14.3 (Me); 47.9 (CH$_2$); 50.4 (CH); 110.9 (C); 122.3 (CH); 124.5 (CH); 126.4 (CH); 130.5 (CH); 147.2 (C); 168.7 (C); 169.3 (C); 201.8 (C). HR-FAB-MS (pos.): 230.1067 (*M*$^+$, $C_{13}H_{14}N_2O_2^+$; calc. 230.1055). Anal. calc. for $C_{13}H_{14}N_2O_2$ (230.26): C 67.81, H 6.13, N 12.17; found: C 68.12, H 6.20, N 12.45.

3.4. *Phenylhydrazine Derivatives* **5a** and **6a**. *Method B* with [Rh(acac)(CO)$_2$] (5 mg, 0.019 mmol, 0.005 equiv.), biphephos (61.4 mg, 0.078 mmol, 0.02 equiv.), **1** (761 mg, 3.8 mmol, 1 equiv.), phenylhydrazine (**4a**; 411 mg, 3.8 mmol, 1 equiv.), 10 bar H_2, and 70 bar CO at 120° for 5 d. The crude product was purified by CC (^{t}BuOMe/cyclohexane 1 : 4): **2**/**3** (6.7%), **5a** (81.3%), and **6a** (8%) as pale yellow oils.

*2-Methyl-3-[4-(2-phenylhydrazinyl)butyl]quinazolin-4(3*H*)-one* (**5a**): ^{1}H-NMR ((D$_6$)DMSO): 1.45 (*quint.*, *J* = 7.3, 2 H); 1.87 (*quint.*, *J* = 7.3, 2 H); 2.21 (*s*, 3 H); 2.44 (*t*, *J* = 7.2, 2 H); 4.09 (*t*, *J* = 7.4, 2 H); 6.29 (*s*, 1 H); 6.30 (*s*, 1 H); 6.74–6.97 (*m*, 5 H); 7.37 (*t*, *J* = 8.1, 1 H); 7.62 (*t*, *J* = 7.8, 1 H); 7.67 (*d*, *J* = 8.0, 1 H); 8.18 (*d*, *J* = 7.2, 1 H). ^{13}C-NMR ((D$_6$)DMSO): 14.2 (Me); 23.9 (CH$_2$); 25.2 (CH$_2$); 36.4 (CH$_2$); 47.3 (CH$_2$); 112.3 (2 CH); 119.4 (CH); 120.2 (C); 126.4 (CH); 126.6 (CH); 126.7 (CH); 129.0 (2 CH); 134.2 (CH); 144.8 (C); 146.4 (C); 161.9 (C); 163.7 (C). HR-FAB-MS (pos.): 322.1810 (*M*$^+$, $C_{19}H_{22}N_4O^+$; calc. 322.1794). Anal. calc. for $C_{19}H_{22}N_4O$ (322.40): C 70.78, H 6.88, N 17.38; found: C 70.67, H 6.81, N 17.65.

*2-Methyl-3-[2-methyl-3-(2-phenylhydrazinyl)propyl]quinazolin-4(3*H*)-one* (**6a**): ^{1}H-NMR ((D$_6$)DMSO): 1.13 (*d*, *J* = 5.7, 3 H); 2.21 (*s*, 3 H); 2.90 (*d*, *J* = 9.5, 2 H); 3.00–3.05 (*m*, 1 H); 3.71 (*d*, *J* = 9.5, 2 H); 6.30 (br. *s*, 2 H); 6.43–6.67 (*m*, 2 H); 7.29–7.33 (*m*, 2 H); 7.44 (*t*, *J* = 7.7, 1 H); 7.60 (*d*, *J* = 8.1, 1 H); 7.66–7.70 (*m*, 3 H). ^{13}C-NMR ((D$_6$)DMSO): 14.2 (Me); 17.8 (Me); 24.3 (CH); 47.2 (CH$_2$); 47.9 (CH$_2$); 112.2 (2 CH); 119.6 (C); 120.1 (CH); 126.1 (CH); 126.7 (CH); 129.0 (CH); 129.7 (2 CH); 134.7 (CH); 145.1 (C); 146.9 (C); 162.2 (C); 163.4 (C). HR-FAB-MS (pos.): 322.1810 (*M*$^+$, $C_{19}H_{22}N_4O^+$; calc. 322.1794). Anal. calc. for $C_{19}H_{22}N_4O$ (322.40): C 70.78, H 6.88, N 17.38; found: C 71.02, H 7.05, N 17.82.

3.5. *(4-Methoxyphenyl)hydrazine Derivatives* **5b** *and* **6b**. Method *B* with [Rh(acac)(CO)$_2$] (5 mg, 0.019 mmol, 0.005 equiv.), biphephos (61.4 mg, 0.078 mmol, 0.02 equiv.), **1** (761 mg, 3.8 mmol, 1 equiv.), (4-methoxyphenyl)hydrazine (**4b**; 525 mg, 3.8 mmol, 1 equiv.), 10 bar H_2, and 70 bar CO at 120° for 5 d. The crude product was purified by CC (^{t}BuOMe/cyclohexane 1 : 4): **2**/**3** (6.8%), **5b** (74.1%), and **6b** (11.1%) as pale yellow oils.

*3-{4-[2-(4-Methoxyphenyl)hydrazinyl]butyl}-2-methylquinazolin-4(3*H*)-one* (**5b**): ^{1}H-NMR (CDCl$_3$): 1.49 (*quint.*, *J* = 7.2, 2 H); 1.79 (*quint.*, *J* = 7.4, 2 H); 2.21 (*s*, 3 H); 2.58 (*t*, *J* = 7.2, 2 H); 3.60 (*s*, 3 H); 4.08 (*t*, *J* = 7.4, 2 H); 6.26 (br. *s*, 2 H); 6.67–6.72 (*m*, 4 H); 7.42 (*t*, *J* = 7.8, 1 H); 7.60 (*d*, *J* = 8.0, 1 H); 7.71 (*t*, *J* = 7.8, 1 H); 7.75 (*d*, *J* = 7.2, 1 H). ^{13}C-NMR (CDCl$_3$): 14.9 (Me); 23.9 (CH$_2$); 26.8 (CH$_2$); 38.4 (CH$_2$); 48.4 (CH$_2$); 54.6 (Me); 114.2 (2 CH); 118.1 (2 CH); 120.6 (C); 126.6 (CH); 126.9 (CH); 127.4 (CH); 134.3 (CH); 144.4 (C); 146.9 (C); 153.9 (C); 162.4 (C); 164.1 (C). HR-FAB-MS (pos.): 352.1923 (*M*$^+$, $C_{20}H_{24}N_4O_2^+$; calc. 352.1899). Anal. calc. for $C_{20}H_{24}N_4O_2$ (352.43): C 68.16, H 6.86, N 15.90; found: C 68.37, H 6.75, N 15.60.

*3-{3-[2-(4-Methoxyphenyl)hydrazinyl]-2-methylpropyl}-2-methylquinazolin-4(3*H*)-one* (**6b**): ^{1}H-NMR (CDCl$_3$): 0.98 (*d*, *J* = 5.6, 3 H); 2.22 (*s*, 3 H); 2.87 (*d*, *J* = 9.5, 2 H); 3.17–3.22 (*m*, 1 H); 3.57 (*s*, 3 H); 3.75 (*d*, *J* = 9.5, 2 H); 6.26 (br. *s*, 2 H); 6.61–6.72 (*m*, 3 H); 7.42 (*t*, *J* = 7.6, 1 H); 7.61 (*d*, *J* = 8.1, 1 H); 7.68–7.74 (*m*, 3 H). ^{13}C-NMR (CDCl$_3$): 14.2 (Me); 17.8 (Me); 24.8 (CH); 47.5 (CH$_2$); 47.9 (CH$_2$); 54.7 (Me); 114.3 (2 CH); 118.5 (2 CH); 120.1 (C); 126.5 (CH); 126.9 (CH); 128.6 (CH); 134.3 (CH); 143.4 (C); 149.4 (C); 153.9 (C); 162.8 (C); 164.2 (C). HR-FAB-MS (pos.): 352.1923 (*M*$^+$, $C_{20}H_{24}N_4O_2^+$; calc. 352.1899). Anal. calc. for $C_{20}H_{24}N_4O_2$ (352.43): C 68.16, H 6.86, N 15.90; found: C 68.02, H 7.05, N 15.82.

3.6. *4-Hydrazinylbenzonitrile Derivatives* **5c** *and* **6c**. *Method B* with [Rh(acac)(CO)$_2$] (5 mg, 0.019 mmol, 0.005 equiv.), biphephos (61.4 mg, 0.078 mmol, 0.02 equiv.), **1** (761 mg, 3.8 mmol, 1 equiv.),

4-hydrazinylbenzonitrile (**4c**; 506 mg, 3.8 mmol, 1 equiv.), 10 bar H_2, and 70 bar CO at 120° for 5 d. The crude product was purified by CC (^{t}BuOMe/cyclohexane 1:4): **2**/**3** (6.8%), **5c** (74%), and **6c** (8.2%) as pale yellow oils.

*4-{2-[4-(2-Methyl-4-oxoquinazolin-3(4*H*)-yl)butyl]hydrazinyl}benzonitrile* (**5c**): ^{1}H-NMR ((D$_6$)DMSO): 1.47 (*quint.*, J = 7.2, 2 H); 1.74 (*quint.*, J = 7.4, 2 H); 2.23 (*s*, 3 H); 2.55 (*t*, J = 7.2, 2 H); 4.06 (*t*, J = 7.4, 2 H); 6.26 (br. *s*, 2 H); 6.82–6.93 (*m*, 4 H); 7.41 (*t*, J = 7.8, 1 H); 7.60 (*d*, J = 8.0, 1 H); 7.69 (*t*, J = 7.8, 1 H); 7.81 (*d*, J = 8.6, 1 H). ^{13}C-NMR ((D$_6$)DMSO): 14.8 (Me); 23.3 (CH$_2$); 26.6 (CH$_2$); 38.1 (CH$_2$); 48.4 (CH$_2$); 96.1 (C); 116.1 (C); 116.3 (2 CH); 119.9 (C); 126.5 (CH); 127.0 (CH); 127.3 (CH); 131.5 (2 CH); 134.2 (CH); 146.9 (C); 152.9 (C); 162.8 (C); 164.3 (C). HR-FAB-MS (pos.): 347.1765 (M^+, $C_{20}H_{21}N_5O^+$; calc. 347.1746). Anal. calc. for $C_{20}H_{21}N_5O$ (347.41): C 69.14, H 6.09, N 20.16; found: C 69.27, H 5.95, N 20.41.

*4-{2-[2-Methyl-3-(2-methyl-4-oxoquinazolin-3(4*H*)-yl)propyl]hydrazinyl}benzonitrile* (**6c**): ^{1}H-NMR ((D$_6$)DMSO): 1.03 (*d*, J = 5.7, 3 H); 2.23 (*s*, 3 H); 2.88 (*d*, J = 9.5, 2 H); 3.23–3.26 (*m*, 1 H); 3.76 (*d*, J = 9.5, 2 H); 6.27 (br. *s*, 2 H); 6.84–6.87 (*m*, 2 H); 7.41 (*t*, J = 7.6, 1 H); 7.61 (*d*, J = 8.1, 1 H); 7.66–7.81 (*m*, 4 H). ^{13}C-NMR ((D$_6$)DMSO): 14.2 (Me); 17.8 (Me); 24.8 (CH); 47.5 (CH$_2$); 47.9 (CH$_2$); 96.1 (C); 116.4 (2 CH); 118.4 (C); 119.8 (C); 126.6 (CH); 126.9 (CH); 128.7 (CH); 132.6 (2 CH); 134.3 (CH); 149.3 (C); 152.0 (C); 163.1 (C); 164.2 (C). HR-FAB-MS (pos.): 347.1765 (M^+, $C_{20}H_{21}N_5O^+$; calc. 347.1746). Anal. calc. for $C_{20}H_{21}N_5O$ (347.41): C 69.14, H 6.09, N 20.16; found: C 68.92, H 6.25, N 20.75.

3.7. *(4-Nitrophenyl)hydrazine Derivatives* **5d** *and* **6d**. *Method B* with [Rh(acac)(CO)$_2$] (5 mg, 0.019 mmol, 0.005 equiv.), biphephos (61.4 mg, 0.078 mmol, 0.02 equiv.), **1** (761 mg, 3.8 mmol, 1 equiv.), (4-nitrophenyl)hydrazine (582 mg, 3.8 mmol, 1 equiv.), 10 bar H_2, and 70 bar CO at 120° for 5 d. The crude product was purified by CC (^{t}BuOMe/cyclohexane 1:4): **2**/**3** (7.2%), **5d** (67.2%), and **6d** (6.6%) as pale yellow oils.

*2-Methyl-3-{4-[2-(4-nitrophenyl)hydrazinyl]butyl}quinazolin-4(3*H*)-one* (**5d**): ^{1}H-NMR ((D$_6$)DMSO): 1.45 (*quint.*, J = 7.3, 2 H); 1.76 (*quint.*, J = 7.3, 2 H); 2.23 (*s*, 3 H); 2.64 (*t*, J = 7.2, 2 H); 4.07 (*t*, J = 7.4, 2 H); 6.26 (br. *s*, 2 H); 7.03–7.07 (*m*, 2 H); 7.42 (*t*, J = 7.8, 1 H); 7.60 (*d*, J = 8.0, 1 H); 7.71–7.76 (*m*, 2 H); 8.03–8.08 (*m*, 2 H). ^{13}C-NMR ((D$_6$)DMSO): 15.0 (Me); 23.4 (CH$_2$); 26.6 (CH$_2$); 38.4 (CH$_2$); 48.4 (CH$_2$); 109.5 (2 CH); 120.3 (C); 123.4 (2 CH); 126.4 (CH); 126.8 (CH); 127.4 (CH); 134.2 (CH); 146.9 (C); 153.4 (C); 154.6 (C); 162.6 (C); 164.1 (C). HR-FAB-MS (pos.): 368.1736 ($[M+H]^+$, $C_{19}H_{22}N_5O_3^+$; calc. 368.1723). Anal. calc. for $C_{19}H_{21}N_5O_3$ (367.40): C 62.11, H 5.76, N 19.06; found: C 62.35, H 5.85, N 19.30.

*2-Methyl-3-{2-methyl-3-[2-(4-nitrophenyl)hydrazinyl]propyl}quinazolin-4(3*H*)-one* (**6d**): ^{1}H-NMR ((D$_6$)DMSO): 0.99 (*d*, J = 5.7, 3 H); 2.23 (*s*, 3 H); 2.88 (*d*, J = 9.5, 2 H); 3.20–3.25 (*m*, 1 H); 3.77 (*d*, J = 9.5, 2 H); 6.28 (br. *s*, 2 H); 6.99–7.03 (*m*, 2 H); 7.43 (*t*, J = 7.6, 1 H); 7.60–7.71 (*m*, 3 H); 8.04–8.07 (*m*, 2 H). ^{13}C-NMR ((D$_6$)DMSO): 14.2 (Me); 17.7 (Me); 24.9 (CH); 47.5 (CH$_2$); 48.5 (CH$_2$); 110.4 (2 CH); 120.1 (C); 123.6 (2 CH); 126.6 (CH); 126.7 (CH); 128.5 (CH); 134.3 (CH); 149.3 (C); 153.8 (C); 154.2 (C); 162.9 (C); 164.2 (C). HR-FAB-MS (pos.): 368.1736 ($[M+H]^+$, $C_{19}H_{22}N_5O_3^+$; calc. 368.1723). Anal. calc. for $C_{19}H_{21}N_5O_3$ (367.40): C 62.11, H 5.76, N 19.06; found: C 61.92, H 5.90, N 18.82.

3.8. *2-Methyl-3-[4-(morpholin-4-yl)butyl]quinazolin-4(3*H*)-one* (**7**). *Method B* with [Rh(acac)(CO)$_2$] (5 mg, 0.019 mmol, 0.005 equiv.), P(OPh)$_3$ (24.2 mg, 0.078 mmol, 0.02 equiv.), **1** (761 mg, 3.8 mmol, 1 equiv.), morpholine (497 mg, 5.7 mmol, 1.5 equiv.), 10 bar H_2, and 60 bar CO at 100° for 5 d. The crude product was purified by CC (CH_2Cl_2/AcOEt 7:3): **7** (89%). Colorless oil. ^{1}H-NMR ($CDCl_3$): 1.40 (*quint.*, J = 7.3, 2 H); 1.62 (*quint.*, J = 7.3, 2 H); 2.22 (*s*, 3 H); 2.36–2.42 (*m*, 4 H); 2.63 (*t*, J = 7.0, 2 H); 3.68–3.74 (*m*, 4 H); 4.09 (*t*, J = 7.4, 2 H); 7.41 (*t*, J = 7.2, 1 H); 7.56–7.74 (*m*, 3 H). ^{13}C-NMR: 14.7 (Me); 22.1 (CH$_2$); 23.2 (CH$_2$); 44.3 (CH$_2$); 54.0 (CH$_2$); 58.1 (2 CH$_2$); 66.9 (2 CH$_2$); 121.1 (C); 125.6 (CH); 126.4 (CH); 126.9 (CH); 134.3 (CH); 147.2 (C); 162.0 (C); 163.9 (C). HR-FAB-MS (pos.): 301.1807 (M^+, $C_{17}H_{23}N_3O_2^+$; calc. 301.1790). Anal. calc. for $C_{17}H_{23}N_3O_2$ (301.38): C 67.75, H 7.69, N 13.94; found: C 67.92, H 7.95, N 13.65.

3.9. *2-Methyl-3-[4-(morpholin-4-ylamino)butyl]quinazolin-4(3*H*)-one* (**8**). *Method B* with [Rh(acac)(CO)$_2$] (5 mg, 0.019 mmol, 0.005 equiv.), P(OPh)$_3$ (24.2 mg, 0.078 mmol, 0.02 equiv.), **1** (761 mg, 3.8 mmol, 1 equiv.), morpholin-4-amine (582 mg, 5.7 mmol, 1.5 equiv.), 10 bar H_2, and 60 bar CO at 100° for 5 d. The crude product was purified by CC (CH_2Cl_2/AcOEt 7:3): **8** (93%). Colorless oil. ^{1}H-NMR

((D$_6$)DMSO): 1.49 (*quint.*, J = 7.4, 2 H); 1.68 (*quint.*, J = 7.2, 2 H); 2.23 (*s*, 3 H); 2.43–2.56 (*m*, 4 H); 2.59 (*s*, 1 H); 3.79–3.93 (*m*, 4 H); 4.07 (*t*, J = 7.4, 2 H); 7.43 (*t*, J = 7.2, 1 H); 7.61–7.76 (*m*, 3 H). ^{13}C-NMR ((D$_6$)DMSO): 14.7 (Me); 22.4 (CH_2); 23.1 (CH_2); 44.4 (CH_2); 52.0 (2 CH_2); 56.6 (CH_2); 63.4 (2 CH_2); 121.3 (C); 125.1 (CH); 125.8 (CH); 126.4 (CH); 134.1 (CH); 146.9 (C); 161.9 (C); 164.3 (C). HR-FAB-MS (pos.): 316.3991 (M^+, $C_{17}H_{24}N_4O_2^+$; calc. 316.1944). Anal. calc. for $C_{17}H_{24}N_4O_2$ (316.40): C 64.53, H 7.65, N 17.71; found: C 64.70, H 7.84, N 17.50.

3.10. *3-{4-{[2-(1*H*-Indol-3-yl)ethyl]amino}butyl}-2-methylquinazolin-4(3*H*)-one* (**9**). *Method B* with [Rh(acac)(CO)$_2$] (5 mg, 0.019 mmol, 0.005 equiv.), P(OPh)$_3$ (24.2 mg, 0.078 mmol, 0.02 equiv.), **1** (761 mg, 3.8 mmol, 1 equiv.), tryptamine (609 mg, 3.8 mmol, 1 equiv.), 10 bar H_2, and 60 bar CO at 100° for 4 d. The crude product was purified by CC (CH_2Cl_2/MeOH 8:2): **9** (78%). Pale yellow oil. ^{1}H-NMR ($CDCl_3$): 1.53 (*quint.* J = 7.4, 2 H); 1.65 (*quint.* J = 7.4, 2 H); 2.25 (*s*, 3 H); 2.61 (*t*, J = 7.1, 2 H); 2.84 (*t*, J = 7.7, 2 H); 3.32 (*t*, J = 7.7, 2 H); 4.08 (*t*, J = 7.4, 2 H); 4.19 (*s*, 1 H); 6.31 (br. *s*, 1 H); 6.72 (*s*, 1 H); 7.13–7.16 (*m*, 2 H); 7.29 (*t*, J = 8.1, 1 H); 7.43 (*t*, J = 7.7, 1 H); 7.54–7.78 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$): 14.7 (Me); 23.1 (2 CH_2); 28.1 (CH_2); 44.3 (CH_2); 47.4 (CH_2); 54.2 (CH_2); 112.2 (CH); 113.3 (C); 118.2 (CH); 119.2 (CH); 120.8 (C); 121.7 (CH); 123.7 (CH); 124.1 (CH); 125.6 (CH); 126.5 (CH); 127.6 (C); 134.4 (CH); 136.5 (C); 147.1 (C); 162.3 (C); 164.1 (C). HR-FAB-MS (pos.): 375.2210 ([M + H]$^+$, $C_{23}H_{27}N_4O^+$; calc. 375.2185). Anal. calc. for $C_{23}H_{26}N_4O$ (374.48): C 73.77, H 7.00, N 14.96; found: C 73.50, H 7.25, N 15.40.

3.11. *3-{4-[(4-Acetylphenyl)amino]butyl}-2-methylquinazolin-4(3*H*)-one* (**10**). *Method B* with [Rh(acac)(CO)$_2$] (5 mg, 0.019 mmol, 0.005 equiv.), P(OPh)$_3$ (24.2 mg, 0.078 mmol, 0.02 equiv.), **1** (761 mg, 3.8 mmol, 1 equiv.), 4-aminoacetophenone (514 mg, 3.8 mmol, 1 equiv.), 10 bar H_2, and 60 bar CO at 120° for 4 d. The crude product was purified by CC (CH_2Cl_2/MeOH 8:2): **10** (67%). Pale yellow oil. ^{1}H-NMR ((D$_6$)DMSO): 1.54 (*quint.*, J = 7.4, 2 H); 1.72 (*quint.*, J = 7.1, 2 H); 2.23 (*s*, 3 H); 2.58 (*t*, J = 7.1, 2 H); 3.29 (*s*, 1 H); 4.09 (*t*, J = 7.4, 2 H); 4.19 (*s*, 1 H); 6.38 (*d*, J = 8.7, 2 H); 7.46 (*t*, J = 7.7, 1 H); 7.63 (*d*, J = 8.0, 1 H); 7.72–7.79 (*m*, 4 H). ^{13}C-NMR ((D$_6$)DMSO): 14.8 (Me); 21.9 (Me); 22.8 (CH_2); 23.6 (CH_2); 44.2 (CH_2); 45.3 (CH_2); 113.7 (2 CH); 120.6 (C); 123.7 (CH); 126.0 (C); 126.2 (CH); 126.5 (CH); 131.6 (2 CH); 134.8 (CH); 148.0 (C); 156.9 (C); 163.2 (C); 164.9 (C); 194.1 (C). HR-FAB-MS (pos.): 349.1813 (M^+, $C_{21}H_{23}N_3O_2^+$; calc. 349.1790). Anal. calc. for $C_{21}H_{23}N_3O_2$ (349.43): C 72.18, H 6.63, N 12.03; found: C 72.50, H 6.36, N 12.35.

4. *Chalcones* **11a** *and* **11b**. A mixture of quinazolinone **10** (10 mmol) and an aromatic aldehyde, *i.e.*, 4-methoxybenzaldehyde or 4-chlorobenzaldehyde (10 mmol), in THF (20 ml) was heated under reflux for 4 h. The solid that separated after concentration and cooling was crystallized from EtOH to give **11a** (73%) and **11b** (65%), resp.

*3-{4-{[4-[(2Z)-3-(4-Methoxyphenyl)-1-oxoprop-2-en-1-yl]phenyl}amino}butyl}-2-methylquinazolin-4(3*H*)-one* (**11a**): M.p. 236–238°. ^{1}H-NMR ((D$_6$)DMSO): 1.58 (*quint.*, J = 7.4, 2 H); 1.71 (*quint.*, J = 7.2, 2 H); 2.22 (*s*, 3 H); 3.09 (*t*, J = 7.2, 2 H); 3.31 (*s*, 1 H); 3.89 (*s*, 3 H); 4.12 (*t*, J = 7.4, 2 H); 6.48 (*d*, J = 8.6, 2 H); 6.93 (*d*, J = 16.8, 1 H); 7.08 (*d*, J = 8.7, 1 H); 7.42 (*t*, J = 7.7, 1 H); 7.60–7.64 (*m*, 4 H); 7.71–7.77 (*m*, 5 H). ^{13}C-NMR ((D$_6$)DMSO): 14.7 (Me); 22.7 (CH_2); 22.9 (CH_2); 42.0 (CH_2); 42.6 (CH_2); 56.5 (Me); 114.5 (2 CH); 114.9 (2 CH); 118.7 (CH); 119.8 (C); 123.7 (CH); 125.7 (CH); 126.0 (CH); 128.8 (C); 130.1 (2 CH); 132.0 (2 CH); 134.4 (CH); 136.9 (C); 144.9 (CH); 147.2 (C); 159.0 (C); 161.1 (C); 162.9 (C); 164.6 (C); 190.7 (C). HR-FAB-MS (pos.): 468.2312 ([M + H]$^+$, $C_{29}H_{30}N_3O_3^+$; calc. 468.2287). Anal. calc. for $C_{29}H_{29}N_3O_3$ (467.56): C 74.50, H 6.25, N 8.99; found: C 74.82, H 6.45, N 9.27.

*3-{4-{[4-[(2Z)-3-(4-Chlorophenyl)-1-oxoprop-2-en-1-yl]phenyl}amino}butyl}-2-methylquinazolin-4(3*H*)-one* (**11b**): M.p. 254–255°. ^{1}H-NMR ((D$_6$)DMSO): 1.55 (*quint.*, J = 7.3, 2 H); 1.70 (*quint.*, J = 7.3, 2 H); 2.22 (*s*, 3 H); 3.07 (*t*, J = 7.1, 2 H); 3.29 (*s*, 1 H); 4.08 (*t*, J = 7.4, 2 H); 6.45 (*d*, J = 8.6, 2 H); 6.87 (*d*, J = 16.7, 1 H); 7.19–7.28 (*m*, 4 H); 7.44 (*t*, J = 7.7, 1 H); 7.62 (*d*, J = 8.1, 1 H); 7.70–7.76 (*m*, 5 H). ^{13}C-NMR ((D$_6$)DMSO): 14.9 (Me); 22.8 (CH_2); 23.2 (CH_2); 42.1 (CH_2); 43.1 (CH_2); 114.8 (2 CH); 118.8 (CH); 120.3 (C); 123.9 (CH); 125.8 (CH); 126.1 (CH); 127.9 (2 CH); 128.5 (2 CH); 128.8 (C); 129.3 (2 CH); 134.3 (CH); 134.4 (C); 135.9 (C); 144.4 (CH); 147.3 (C); 158.9 (C); 163.1 (C); 164.6 (C); 190.7 (C). HR-FAB-MS (pos.): 472.1817 ([M + H]$^+$, $C_{28}H_{27}ClN_3O_2^+$; calc. 472.1792). Anal. calc. for $C_{28}H_{26}ClN_3O_2$ (471.98): C 71.25, H 5.55, Cl 7.51, N 8.90; found: C 71.54, H 5.78, Cl 7.18, N 9.21.

5. *Pyrazoles* **12a** *and* **12b**. A soln. of **11a** or **11b** (10 mmol) and $N_2H_4 \cdot H_2O$ (15 mmol) in EtOH (20 ml) was heated under reflux for 6 h. The solid that separated after concentration and cooling was

filtered off, washed with petroleum ether (60–80°) and recrystallized from the proper solvent to afford **12a** (74%) and **12b** (79%), resp.

*3-{4-{[4-[5-(4-Methoxyphenyl)-1*H*-pyrazol-3-yl]phenyl}amino}butyl}-2-methylquinazolin-4(3*H*)-one* (**12a**): M.p. 211–213° (toluene). ^{1}H-NMR ((D$_6$)DMSO): 1.58 (*quint.*, *J* = 7.3, 2 H); 1.71 (*quint.*, *J* = 7.3, 2 H); 2.24 (*s*, 3 H); 3.06 (*t*, *J* = 7.1, 2 H); 3.19 (*s*, 1 H); 3.92 (*s*, 3 H); 4.13 (*t*, *J* = 7.4, 2 H); 6.25 (*d*, *J* = 8.6, 2 H); 6.68 (*s*, 1 H); 7.06–7.11 (*m*, 2 H); 7.21 (*s*, 1 H); 7.42–7.46 (*m*, 2 H); 7.63 (*d*, *J* = 7.9, 1 H); 7.73–7.82 (*m*, 5 H). ^{13}C-NMR ((D$_6$)DMSO): 14.9 (Me); 22.9 (CH$_2$); 23.0 (CH$_2$); 42.2 (CH$_2$); 42.6 (CH$_2$); 55.9 (Me); 102.5 (CH); 116.5 (2 CH); 119.5 (CH); 119.8 (C); 123.6 (CH); 126.1 (CH); 126.4 (2 CH); 127.2 (2 CH); 129.3 (C); 130.3 (2 CH); 130.9 (C); 134.3 (CH); 146.8 (C); 147.7 (C); 148.4 (C); 158.8 (C); 161.1 (C); 163.7 (C); 164.3 (C). HR-FAB-MS (pos.): 480.2416 ([*M* + H]$^+$, $C_{29}H_{30}N_5O_2^+$; calc. 480.2400). Anal. calc. for $C_{29}H_{29}N_5O_2$ (479.57): C 72.63, H 6.10, N 14.60; found: C 72.32, H 5.75, N 14.25.

*3-{4-{[4-[5-(4-Chlorophenyl)-1*H*-pyrazol-3-yl]phenyl}amino}butyl}-2-methylquinazolin-4(3*H*)-one* (**12b**): M.p. 218–219° (EtOH). ^{1}H-NMR ((D$_6$)DMSO): 1.61 (*quint.*, *J* = 7.2, 2 H); 1.73 (*quint.*, *J* = 7.3, 2 H); 2.23 (*s*, 3 H); 3.07 (*t*, *J* = 7.1, 2 H); 3.22 (*s*, 1 H); 4.09 (*t*, *J* = 7.4, 2 H); 6.27 (*d*, *J* = 8.7, 2 H); 6.70 (*s*, 1 H); 7.26 (*s*, 1 H); 7.32–7.42 (*m*, 4 H); 7.61 (*d*, *J* = 8.1, 1 H); 7.68–7.74 (*m*, 3 H); 7.80–7.84 (*m*, 2 H). ^{13}C-NMR ((D$_6$)DMSO): 14.9 (Me); 22.7 (CH$_2$); 23.2 (CH$_2$); 42.2 (CH$_2$); 43.2 (CH$_2$); 103.9 (CH); 115.1 (2 CH); 119.9 (C); 124.0 (CH); 125.9 (2 CH); 128.2 (4 CH); 130.5 (2 CH); 131.2 (C); 134.1 (C); 134.3 (CH); 136.2 (C); 147.3 (C); 148.1 (C); 148.5 (C); 159.4 (C); 163.5 (C); 164.4 (C). HR-FAB-MS (pos.): 484.1927 ([*M* + H]$^+$, $C_{28}H_{27}ClN_5O^+$; calc. 484.1904). Anal. calc. for $C_{28}H_{26}ClN_5O$ (483.99): C 69.48, H 5.41, Cl 7.33, N 14.47; found: C 69.90, H 5.75, Cl 7.05, N 14.80.

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Received May 8, 2012