59. A Novel Approach to 2,2-Disubstituted 1,2-Dihydro-4-phenylquinolines

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The reaction of 2-(1-phenylvinyl)aniline and 4-chloro-2-(1-phenylvinyl)aniline with acetophenone derivatives, 1-(naphthalen-1-yl)ethanone and 1-(furan-2-yl)ethanone in toluene at 110–115° with toluene-4-sulfonic acid as a catalyst leads in good-to-excellent yields to the 2,2-disubstituted 1,2-dihydro-4-phenyl-quinolines **1**–**18** (*Scheme 1*, *Table*). The structure of the new racemic 1,2-dihydroquinolines **1**–**18** is determined by NMR spectroscopy. A reaction mechanism proceeding *via* a 6π-electrocyclic rearrangement of 2-(1-phenylvinyl)anils **19** as the key step is proposed for the formation of these compounds (*Scheme 1*). The scope and limitations of the novel method are discussed (*Scheme 2*).

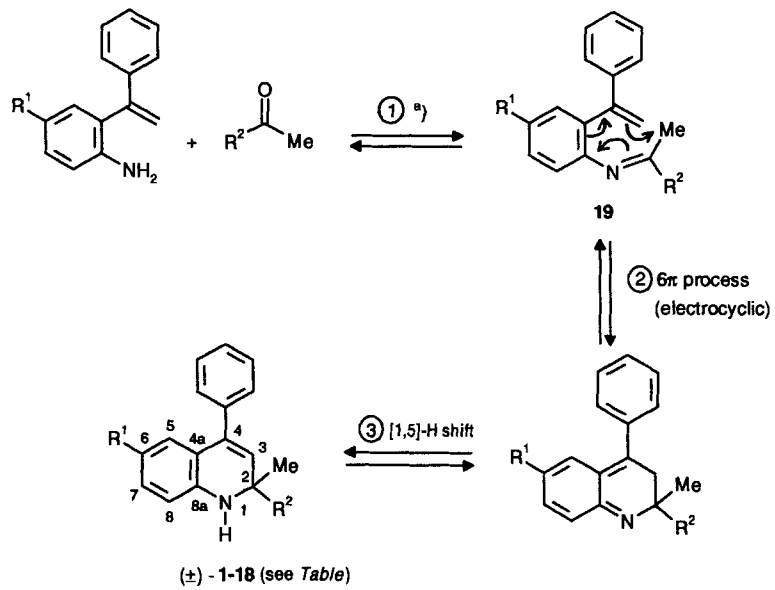
1. Introduction. – For the synthesis of N-heterocycles such as quinolines [1–3], cinnolines [4–6], quinolin-2-ones [7], and octahydropyrido[4′,3′:1,4]cyclobut[1,2-*b*]indoles [8], 2-vinylaniline and 2-(1-phenylvinyl)aniline derivatives are important starting materials. In this paper, we describe the use of 2-(1-phenylvinyl)anilines in the synthesis of a series of new and interesting 1,2-dihydro-4-phenyl-quinolines.

2. Results. – In the last few years, α-vinylanils have become well accepted intermediates in the formation of quinoline derivatives [2] [3] [9] [10]. To investigate the utility of α-vinylanils for the synthesis of 2,2-disubstituted 1,2-dihydroquinoline derivatives, the acid-catalyzed reaction of 2-(1-phenylvinyl)aniline derivatives with acylated aromatic and heterocyclic compounds was studied. The 1,2-dihydroquinolines can be expected to be formed through the intermediacy of α-vinylanils, which may be isolated or converted *in situ* to the final products. As a first interesting result of these investigations, we report here on the toluene-4-sulfonic-acid (TsOH) catalyzed reaction of several 2-(1-phenylvinyl)anilines with acetophenone derivatives and 1-(naphthalen-1-yl)ethanone, which turned out to be a high-yielding novel approach to 2,2-disubstituted 1,2-dihydro-4-phenylquinolines (*Scheme 1*, *Table*). The *Table* clearly shows that the yields are generally high and independent of the chosen starting aniline derivative. Furthermore, it can be seen that the reaction process tolerates many functional groups. The reduced yield in the case of 1-(furan-2-yl)ethanone is probably due to the instability of the furan ring under the acidic reaction conditions. The new 1,2-dihydro-4-phenyl-quinolines are identified by ^{1}H- and ^{13}C-NMR spectroscopy (see *Exper. Part*).

The 1,2-dihydroquinolines of the new type can be viewed as potential rubber additives [11], dye-stuff intermediates [10] [12] [13], or starting materials for the synthesis of more complicated 1,2-dihydroquinoline derivatives with potential biological activity [14].

3. Discussion. – To our knowledge, among the known methods for the synthesis of 1,2-dihydroquinolines [15–18], only one provides asymmetrically 2,2-disubstituted 1,2-dihydro-4-phenylquinolines [18]. In this approach, lithium anilides and phenylacetylene

Scheme 1



(±) - **1-18** (see *Table*)

R^1 = H, Cl
R^2 = Ph, subst. phenyl, naphthalen-1-yl, furan-2-yl

[a]) TsOH, toluene, 6–16 h, 110–115°.

Table. *Acid-Catalyzed Reactions of 2-(1-Phenylvinyl)anilines with Acetophenone Derivatives, 1-(Naphthalen-1-yl)ethanone, and 1-(Furan-2-yl)ethanone*[a])[b])[c])

R^1	R^2	Reaction time [h]	Product	Yield [%]
H	Phenyl	8	**1**	90
H	2-Fluorophenyl	6	**2**	92
H	2-Methoxyphenyl	15	**3**	67
H	3-(Trifluoromethyl)phenyl	6	**4**	86
H	4-Fluorophenyl	12	**5**	92
H	4-Chlorophenyl	15	**6**	81
H	4-Hydroxyphenyl	8	**7**	89
H	4-Methoxyphenyl	8	**8**	81
H	2,4-Dimethylphenyl	16	**9**	80
H	3,4-Dimethoxyphenyl	6	**10**	96
H	3,5-Difluorophenyl	7	**11**	72
H	Naphthalen-1-yl	12	**12**	75
H	Furan-2-yl	12	**13**	40
Cl	Phenyl	15	**14**	89
Cl	4-Chlorophenyl	15	**15**	87
Cl	4-Hydroxyphenyl	8	**16**	88
Cl	4-Nitrophenyl	15	**17**	86
Cl	4-Methoxyphenyl	15	**18**	91

[a]) The reaction conditions are not optimized. In all cases, TsOH was used as catalyst and the reaction carried out in refluxing toluene.

[b]) In some cases, (2-aminophenyl)phenylmethanols instead of 2-(1-phenylvinyl)anilines were used without significant loss of yield.

[c]) For the synthesis of 2-(1-phenylvinyl)aniline and 4-chloro-2-(1-phenylvinyl)aniline, see [4] and [6].

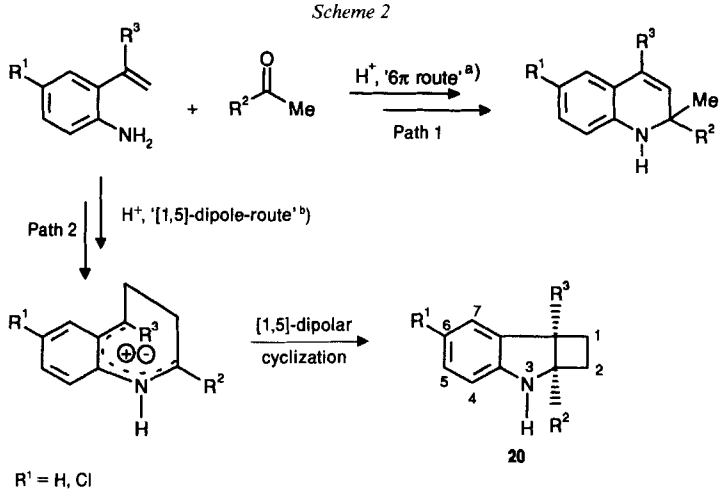
are used as starting materials, leading to 1,2-dihydro-2-methyl-2,4-diphenylquinolines in 40–50% yield. This method, however, has its limitations: *e.g.* 1,2-dihydroquinolines with various aryl moieties in the 2- and 4-position are not available. Our new and simple approach, in which we use 2-(1-phenylvinyl)anilines and acylated aromatic or heterocyclic compounds as starting materials, with TsOH as catalyst, has three advantages in comparison with the known method: *1*) simpler handling (avoidance of organolithium compounds and $SnCl_4$), *2*) higher yields, and *3*) much broader scope.

For the described formation of 1,2-dihydro-4-phenylquinolines, we propose a reaction mechanism, proceeding *via* anil formation, 6π-electrocyclic rearrangement, and [1,5]-H shift (see *Scheme 1*). In this mechanistic proposal, the presence of an acid seems only to be necessary for the formation of the imine **19**; however, cationic species such as iminium ions may also be considered as intermediates. Upon investigation of the acid-catalyzed reaction of 2-isopropenlyaniline (R^3 = Me) with acylated aromatic or heterocyclic compounds, a first limitation of the new method was discovered. These reactions generally took an unselective course and either gave unseparable mixtures of 1,2-dihydroquinolines and 2,2a,3,7b-tetrahydro-1*H*-cycobut[*b*]indoles **20** (R^2 = 3-methoxyphenyl, 4-nitrophenyl, 2,4-dimethylphenyl) or only **20** (R^2 = phenyl, furan-2-yl, pyridin-2-yl) in poor isolated yields of 20–25% (*Scheme 2*), indicating that in these cases the '[1,5]-dipole route' competes with the '6π route' [8] [9].

The new cyclobut[*b*]indoles are also of considerable interest, because approaches to these types of compounds are limited. In fact, only a photochemically induced [2 + 2] cycloaddition is known as a route to 3*H*-cyclobut[*b*]indoles [19–21]. As photochemical processes often turn out to be preparatively problematic (low yields, difficult control of regioselectivity), this new '[1,5]-dipole approach' may offer a useful alternative method.

Further work in this area in the authors laboratory is in progress in the expectation that an understanding of the detailed mechanism of the '6π route' and the '[1,5]-dipole

Scheme 2



R^1 = H, Cl
R^2 = Ph, 2,4-dimethylphenyl, 3-methoxyphenyl, 4-nitrophenyl, furan-2-yl, pyridin-2-yl
R^3 = Me

[a]) For the mechanism of the '6π route', see [8] [9]. [b]) For the mechanism of the '[1,5]-dipole route', see [8].

route' will result in further progress in the methodology of the synthesis of 1,2-dihydroquinolines and cyclobut[*b*]indoles, using 2-(1-vinyl)anilines as starting materials.

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Experimental Part

General. See [8] [9]. *1,2-Dihydro-4-phenylquinoline Derivatives*: *General Procedure.* A mixture of 0.01M 2-(1-phenylvinyl)aniline or 4-chloro-2-(1-phenylvinyl)aniline, 0.01–0.013M ketone (*Fluka* or *Aldrich*), TsOH (*Merck*; 0.10 g) and abs. toluene (15 ml) was heater under reflux (*Dean-Stark* trap) for 6–16 h (see *Table*). The mixture was evaporated and the residue purified either by flash chromatography (FC; SiO_2, AcOEt/hexane 1:4 to 1:13) or by recrystallization of the corresponding hydrochlorides, which were prepared by adding *ca.* 4.5N HCl/EtOH (10 ml) to the evaporated residues. In some cases, both purification methods were used to obtain anal. pure samples ($\geq 99\%$).

(±)-1,2-Dihydro-2-methyl-2,4-diphenylquinoline (**1**): Purified by FC (AcOEt/hexane 1:12). Yellow crystals. M.p. 113–115° ([18]: 112–113°). IR (KBr): 3369*m*, 3055*m*, 3024*w*, 2976*w*, 1626*m*, 1597*m*, 1489*s*, 1466*s*, 1423*w*, 1113*m*, 1273*m*, 1217*m*, 1128*m*, 1074*m*, 851*m*, 771*s*, 754*s*, 727*m*, 696*s*. ^{1}H-NMR ($CDCl_3$): 1.79 (*s*, Me–C(2)); 4.21 (*s*, NH); 5.65 (*s*, H–C(3)); 6.55–6.60 (*m*, H–C(6), H–C(8)); 6.92 (*dd*, J = 8.0, 1.0, H–C(5)); 7.06 (*td*, J = 8.0, 1.0, H–C(7)); 7.25 (*tm*, H–C(4′)); 7.30–7.40 (*m*, 7 arom. H); 7.55–7.60 (*m*, 2 arom. H). ^{13}C-NMR (^{1}H-coupled; $CDCl_3$): 30.04 (*qd*, Me–C(2)); 56.97 (*m*, C(2)); 113.12 (*dd*, C(8)); 117.14 (*dd*, C(6)); 120.11 (*m*, C(4a)); 125.26 (*m*, C(2′), C(6′)); 126.05 (*m*, C(5) or C(7)); 126.72 (*m*, C(4′)); 127.29 (*m*, C(3)); 128.10 (*m*, C(3″), C(5″)); 128.32 (*m*, C(3′), C(5′)); 128.89 (*m*, C(4″)); 128.91 (*m*, C(2″), C(6″)); 129.0 (*m*, C(5) or C(7)); 135.60 (*s*, C(4)); 139.35 (*m*, C(1″)); 143.12 (*t*, C(8a)); 148.73 (*m*, C(1′)). MS: 297 (8, M^+), 283 (30), 282 (100), 220 (42), 204 (22), 176 (11), 141 (16).

(±)-2-(2-Fluorophenyl)-1,2-dihydro-2-methyl-4-phenylquinoline (**2**): Purified by FC (AcOEt/hexane 1:9) and recrystallization of the free amine from cyclohexane. Yellow crystals. M.p. 105–107°. IR (KBr): 3385*s*, 3375*s*, 3053*w*, 3026*w*, 2976*w*, 1628*m*, 1599*m*, 1576*w*, 1481*s*, 1375*w*, 1275*m*, 1219*s*, 1153*w*, 1128*w*, 1036*m*, 771*s*, 752*s*, 706*s*. ^{1}H-NMR ($CDCl_3$): 1.84 (*s*, Me–C(2)); 4.67 (*s*, NH); 5.93 (*s*, H–C(3)); 6.58 (*td*, J = 8.0, 1.0, H–C(6)); 6.67 (*dd*, J = 8.0, 1.0, H–C(8)); 6.89 (*dd*, J = 8.0, 1.0, H–C(5)); 7.0–7.10 (*m*, 3 arom. H); 7.20 (*m*, arom. H); 7.33–7.46 (*m*, 6 arom. H). ^{13}C-NMR (^{1}H-coupled; $CDCl_3$): 30.33 (*qd*, Me–C(2)); 55.79 (*m*, C(2)); 113.44 (*dd*, C(8)); 116.29 (*dd*, C(3′)); 117.70 (*dd*, C(6)); 120.80 (*m*, C(4a)); 123.82 (*ddd*, C(4′)); 126.20 (*m*, C(5), or C(7)); 127.09 (*m*, C(5′)); 127.23 (*m*, C(3)); 127.45 (*m*, C(5) or C(7)); 128.15 (*m*, C(3″), C(5″)); 128.50 (*m*, C(6′)); 128.82 (*m*, C(4″)); 128.93 (*m*, C(2″), C(6″)); 134.85 (*m*, C(1′)); 137.04 (*s*, C(4)); 139.30 (*m*, C(1″)); 143.33 (*t*, C(8a)); 159.65 (*tdd*, C(2′)). MS: 315 (8, M^+), 300 (100), 220 (28), 204 (21), 139 (23).

(±)-1,2-Dihydro-2-(2-methoxyphenyl)-2-methyl-4-phenylquinoline (**3**): Purified by FC (AcOEt/hexane 1:12). Yellow crystals. M.p. 115–117°. IR (KBr): 3387*m*, 3053*w*, 2974*w*, 2928*w*, 1641*w*, 1601*s*, 1580*w*, 1487*s*, 1369*m*, 1319*m*, 1283*m*, 1234*s*, 1180*m*, 1124*m*, 1022*s*, 806*m*, 764*m*, 743*s*, 700*s*. ^{1}H-NMR ($CDCl_3$): 1.82 (*s*, Me–C(2)); 3.97 (*s*, MeO–C(2′)); 5.43 (*s*, NH); 5.92 (*s*, H–C(3)); 6.52 (*td*, J = 8.0, 1.0, H–C(6)); 6.56 (*dd*, J = 8.0, 1.0, H–C(8)); 6.84 (*dd*, J = 8.0, 1.0, arom. H); 6.85 (*td*, J = 8.0, 1.0, arom. H); 6.92 (*d*, J = 8.0, arom. H); 6.98 (*td*, J = 8.0, 1.0, H–C(7)); 7.18 (*td*, J = 8.0, 1.0, arom. H; 7.34–7.48 (*m*, 6 arom. H). ^{13}C-NMR (^{1}H-coupled; $CDCl_3$): 30.22 (*qd*, Me–C(2)); 52.22 (*q*, MeO–C(2′)); 56.40 (*sext.*, C(2)); 111.57 (*dd*, C(3′)); 113.49 (*dd*, C(8)); 117.23 (*dd*, C(6)); 120.47 (*ddd*, C(5′)); 121.10 (*q*, C(4a)); 126.01 (*ddd*, C(5) or C(7)); 127.15 (*ddd*, C(4′) or C(6′)); 127.35 (*dt*, C(4″)); 127.91 (*dd*, C(4′) or C(6′)); 128.16 (*dd*, C(3″), C(5″)); 128.31 (*dq*, C(3)); 128.49 (*ddd*, C(5) or C(7)); 128.97 (*dt*, C(2″), C(6″)); 135.39 (*m*, C(4)); 136.89 (*m*, C(1′)); 139.80 (*q*, C(1″)); 144.24 (*t*, C(8a)); 156.60 (*m*, C(2′)). MS: 327 (7, M^+), 313 (36), 312 (100), 297 (27), 296 (24), 220 (38).

(±)-1,2-Dihydro-2-methyl-4-phenyl-2-(3-trifluoromethylphenyl)quinoline (**4**): Purified by FC (AcOEt/hexane 1:9) and recrystallization of the hydrochloride from cyclohexane/Et_2O 10:1. Slightly greenish crystals. M.p. 89–91°. IR (KBr): 3369*s*, 3055*w*, 2978*w*, 2928*w*, 1626*m*, 1601*m*, 1489*m*, 1468*s*, 1448*m*, 1375*m*, 1335*s*, 1292*w*, 1169*s*, 1132*s*, 1070*m*, 899*m*, 847*m*, 802*m*, 771*s*, 758*s*, 702*s*. ^{1}H-NMR ($CDCl_3$): 1.81 (*s*, Me–C(2)); 4.20 (*s*, NH); 5.62 (*s*, H–C(3)); 6.60 (*t*, J = 8.0, H–C(6)); 6.61 (*d*, J = 8.0, H–C(8)); 6.92 (*dd*, J = 8.0, 1.0, H–C(5)); 7.07 (*td*, J = 8.0, 1.0, H–C(7)); 7.30–7.40 (*m*, 5 arom. H); 7.46 (*t*, J = 8.0, H–C(5′)); 7.50 (*d*, J = 8.0, H–C(6′)); 7.79 (*dm*, J = 8.0, H–C(4′)); 7.81 (*s*, H–C(2′)). ^{13}C-NMR (^{1}H-coupled; $CDCl_3$): 29.78 (*qd*, Me–C(2)); 56.99 (*m*, C(2)); 113.42 (*dd*, C(8)); 117.68 (*dd*, C(6)); 120.17 (*q*, C(4a)); 122.0 (*dm*, C(2′)); 123.70 (*dm*, C(4′)); 124.20 (*m*, CF_3–C(3′)); 126.31 (*m*, arom. C); 127.57 (*m*, arom. C); 128.13 (*m*, arom. C); 128.25 (*m*, C(3″), C(5″)); 128.93 (*m*, C(2″), C(6″)); 129.13 (*m*,

arom. C); 129.20 (*m*, arom. C); 130.56 (*m*, C(3′)); 136.41 (*s*, C(4)); 139.08 (*qm*, C(1″)); 142.83 (*t*, C(8a)); 149.82 (*m*, C(1′)). MS: 365 (8, M^+), 350 (100), 220 (42), 204 (16).

(±)-2-(4-Fluorophenyl)-1,2-dihydro-2-methyl-4-phenylquinoline (**5**): Purified by FC (AcOEt/hexane 1:7) and recrystallization of the free amine from cyclohexane. White powder. M.p.88–90°. IR (KBr): 3366*s*, 3055*w*, 3026*w*, 2978*w*, 1626*m*, 1601*s*, 1506*s*, 1464*s*, 1423*w*, 1312*m*, 1232*m*, 1161*w*, 831*s*, 773*s*, 764*s*, 706*m*. ^{1}H-NMR ($CDCl_3$): 1.77 (*s*, Me–C(2)); 4.16 (*s*, NH); 5.58 (*s*, H–C(3)); 6.55–6.60 (*m*, H–C(6), H–C(8)); 6.90 (*dd*, J = 8.0, 1.0, H–C(5)); 6.98–7.07 (*m*, H–C(7), H–C(3′), H–C(5′)); 7.30–7.40 (*m*, 5 arom. H); 7.52 (*m*, H–C(2′), H–C(6′)). ^{13}C-NMR (^{1}H-coupled; $CDCl_3$): 30.0 (*qd*, Me–C(2)); 56.67 (*m*, C(2)); 113.25 (*dd*, C(8)); 115.07 (*ddd*, C(3′), C(5′)); 117.41 (*dd*, C(6)); 120.13 (*m*, C(4a)); 126.20 (*ddd*, C(5) or C(7)); 127.13 (*dd*, C(2′), C(6′)); 127.48 (*m*, C(3)); 128.24 (*m*, C(3″), C(5″)); 128.85 (*m*, C(4″)); 128.97 (*m*, C(2″), C(6″)); 129.06 (*m*, C(5) or C(7)); 135.81 (*s*, C(4)); 139.28 (*m*, C(1″)); 143.00 (*t*, C(8a)); 144.66 (*m*, C(1′)); 161.66 (*m*, C(4′)). MS: 315 (6, M^+), 300 (100), 220 (34), 204 (28), 176 (14), 149 (20), 140 (22), 139 (25).

(±)-2-(4-Chlorophenyl)-1,2-dihydro-2-methyl-4-phenylquinoline (**6**): Purified by FC (AcOEt/hexane 1:12). Slightly reddish powder. M.p. 105–107°. IR (KBr): 3391*m*, 3040*w*, 3026*w*, 2926*w*, 1639*m*, 1599*s*, 1474*s*, 1394*w*, 1373*w*, 1313*m*, 1092*s*, 1010*m*, 827*s*, 771*s*, 748*s*, 702*s*. ^{1}H-NMR ($CDCl_3$): 1.75 (*s*, Me–C(2)); 4.17 (*s*, NH); 5.59 (*s*, H–C(3)); 6.55–6.60 (*m*, H–C(6), H–C(8)); 6.90 (*dd*, J = 8.0, 1.0, H–C(5)); 7.04 (*td*, J = 8.0, 1.0, H–C(7)); 7.30–7.40 (*m*, 7 arom. H); 7.49 (*dm*, J = 9.0, 2 arom. H). ^{13}C-NMR (^{1}H-coupled; $CDCl_3$): 29.96 (*qd*, Me–C(2)); 56.65 (*m*, C(2)); 113.24 (*dd*, C(8)); 117.45 (*dd*, C(6)); 120.12 (*q*, C(4a)); 126.20 (*m*, C(5) or C(7)); 126.81 (*m*, C(2′), C(6′)); 127.47 (*m*, arom. C); 128.19 (*m*, C(3′), C(5′)); 128.42 (*m*, C(3″), C(5″)); 128.66 (*m*, arom. C); 128.90 (*m*, C(2″), C(6″)); 129.08 (*m*, C(5) or C(7)); 132.54 (*tt*, C(4′)); 136.0 (*s*, C(4)); 139.15 (*q*, C(1″)); 142.91 (*t*, C(8a)); 147.30 (*m*, C(1′)). MS: 331 (5, M^+(^{35}Cl)), 318 (34), 316 (100), 220 (36), 204 (26), 176 (12), 139 (21).

(±)-1,2-Dihydro-2-(4-hydroyphenyl)-2-methyl-4-phenylquinoline (**7**): Purified by FC (AcOEt/hexane 1:7). White crystals. M.p. 146–148°. IR (KBr): 3551*s*, 3362*s*, 3055*w*, 3028*w*, 2980*w*, 1622*m*, 1601*m*, 1510*s*, 1462*s*, 1448*m*, 1304*w*, 1263*s*, 1190*m*, 1173*m*, 851*w*, 827*s*, 773*s*, 764*s*, 706*s*. ^{1}H-NMR ($CDCl_3$): 1.77 (*s*, Me–C(2)); 4.15 (*s*, NH); 4.90 (*s*, OH); 5.60 (*s*, H–C(3)); 6.54 (*dd*, J = 8.0, 1.0, H–C(8)); 6.57 (*td*, J = 8.0, 1.0, H–C(6)); 6.78 (*dt*, J = 8.0, 1.0, H–C(3′), H–C(5′)); 6.92 (*dd*, J = 8.0, 1.0, H–C(5)); 7.03 (*td*, J = 8.0, H–C(7)); 7.32–7.40 (*m*, 5 arom. H); 7.43 (*dm*, J = 8.0, H–C(2′), H–C(6′)). ^{13}C-NMR (^{1}H-coupled; $CDCl_3$): 26.39 (*qm*, Me–C(2)); 55.67 (*m*, C(2)); 113.20 (*dd*, C(8)); 114.81 (*dd*, C(3′), C(5′)); 115.53 (*dd*, C(6)); 119.28 (*m*, C(4a)); 125.09 (*m*, C(5) or C(7)); 126.29 (*m*, C(2′), C(6′)); 127.39 (*m*, C(3)); 128.35 (*m*, C(3″), C(5″)); 128.71 (*m*, C(4″)); 129.61 (*m*, C(5) or C(7)); 134.63 (*s*, C(4)); 139.27 (*q*, C(1″)); 140.30 (*m*, C(1′)); 144.71 (*t*, C(8a)); 155.86 (*tm*, C(4′)). MS: 313 (6, M^+), 220 (28), 204 (16), 176 (10).

(±)-1,2-Dihydro-2-(4-methoxyphenyl)-2-methyl-4-phenylquinoline (**8**): Purified by FC (AcOEt/hexane 1:12). Yellow powder. M.p. 91–92°. IR (KBr): 3368*s*, 3053*w*, 3024*w*, 2972*w*, 1601*s*, 1510*s*, 1462*s*, 1298*w*, 1251*s*, 1178*s*, 825*s*, 773*s*, 701*m*. ^{1}H-NMR ($CDCl_3$): 1.77 (*s*, Me–C(2)); 3.79 (*s*, MeO–C(4′)); 4.14 (*s*, NH); 5.59 (*s*, H–C(3)); 6.55 (*m*, H–C(6), H–C(8)); 6.87 (*dm*, J = 8.0, H–C(3′), H–C(5′)); 6.91 (*dd*, J = 8.0, 1.0, H–C(5)); 7.02 (*td*, J = 8.0, 1.0, H–C(7)); 7.30–7.40 (*m*, 5 arom. H); 7.48 (*dm*, J = 8.0, H–C(2′), H–C(6′)). ^{13}C-NMR (^{1}H-coupled; $CDCl_3$): 29.92 (*qd*, Me–C(2)); 55.17 (*q*, MeO–C(4′)); 56.54 (*m*, C(2)); 113.14 (*dd*, C(8)); 113.63 (*dd*, C(3′), C(5′)); 117.10 (*dd*, C(6)); 120.10 (*q*, C(4a)); 126.04 (*ddd*, C(5) or C(7)); 126.60 (*dd*, C(2′), C(6′)); 127.33 (*m*, C(3)); 128.16 (*m*, C(3″), C(5″)); 128.90 (*m*, C(4″)); 128.97 (*m*, C(2″), C(6″)); 129.35 (*m*, C(5) or C(7)); 135.38 (*s*, C(4)); 139.44 (*m*, C(1″)); 141.10 (*m*, C(1′)); 143.18 (*t*, C(8a)); 158.36 (*m*, C(4′)). MS: 327 (7, M^+), 313 (28), 312 (100), 269 (12), 220 (28), 156 (11).

(±)-2-(2,4-Dimethylphenyl)-1,2-dihydro-2-methyl-4-phenylquinoline (**9**): Purified by FC (AcOEt/hexane 1:12). Yellow powder. M.p. 90–92°. IR (KBr): 3383*s*, 3020*w*, 2964*m*, 2920*w*, 1634*m*, 1599*s*, 1493*s*, 1471*s*, 1423*m*, 1317*s*, 1252*m*, 1204*m*, 1072*m*, 1038*m*, 816*m*, 771*s*, 744*s*, 702*s*. ^{1}H-NMR ($CDCl_3$): 1.83 (*s*, Me–C(2)); 2.31 (*s*, Me–C(4′)); 2.61 (*s*, Me–C(2′)); 4.17 (*s*, NH); 5.49 (*s*, H–C(3)); 6.48 (*dd*, J = 8.0, 1.0, H–C(8)); 6.55 (*td*, J = 8.0, 1.0, H–C(6)); 6.92 (*dd*, J = 8.0, 1.0, H–C(5)); 6.98 (*d*, J = 8.0, H–C(5′) or H–C(6′)); 7.02 (*m*, H–C(3′), H–C(5′)); 7.30–7.41 (*m*, 6 arom. H). ^{13}C-NMR (^{1}H-coupled; $CDCl_3$): 20.67 (*qt*, Me–C(4′)); 22.47 (*qd*, Me–C(2′)); 29.55 (*q*, Me–C(2)); 57.53 (*m*, C(2)); 112.87 (*dd*, C(8)); 116.66 (*dd*, C(6)); 119.63 (*q*, C(4a)); 125.08 (*d*, C(6′)); 125.87 (*d quint.*, C(5′)); 126.18 (*ddd*, C(5) or C(7)); 127.21 (*m*, C(3)); 128.14 (*dd*, C(3″), C(5″)); 128.31 (*m*, C(5) or C(7)); 128.81 (*m*, C(2″) or C(6″)); 128.91 (*m*, C(4″)); 133.66 (*d sext.*, C(3′)); 135.55 (*s*, C(4)); 137.04 (*qd*, C(2′)); 138.71 (*quint.*, C(4)); 139.62 (*qm*, C(1″)); 141.79 (*m*, C(1′)); 143.18 (*t*, C(8a)). MS: 325 (6, M^+), 311 (34), 310 (100), 220 (50), 204 (18), 148 (11).

(±)-2-(3,4-Dimethoxyphenyl)-1,2-dihydro-2-methyl-4-phenylquinoline (**10**): Purified by FC (AcOEt/hexane 1:4). Yellow resin. IR (KBr): 3368*m*, 2961*w*, 2930*w*, 1601*m*, 1516*s*, 1464*s*, 1408*m*, 1319*w*, 1258*s*, 1146*s*, 1026*s*, 808*w*, 770*s*, 748*s*, 700*m*. ^{1}H-NMR ($CDCl_3$): 1.78 (*s*, Me–C(2)); 3.84 (*s*, MeO–C(3′) or MeO–C(4′)); 3.86 (*s*, MeO–C(3′) or MeO–C(4′)); 4.16 (*s*, NH); 5.60 (*s*, H–C(3)); 6.58 (*m*, H–C(6), H–C(8)); 6.83 (*d*, J = 8.0,

H–C(5')); 6.92 (*dd*, *J* = 8.0, 1.0, H–C(5)); 7.02 (*td*, *J* = 8.0, 1.0, H–C(7)); 7.07 (*dd*, *J* = 8.0, 2.0, H–C(6')); 7.17 (*d*, *J* = 2.0, H–C(2')); 7.30–7.41 (*m*, 5 arom. H). ^{13}C-NMR (^{1}H-coupled; $CDCl_3$): 29.24 (*qd*, Me–C(2)); 55.60 (*q*, MeO–C(3'), MeO–C(4')); 56.56 (*m*, C(2)); 109.42 (*dd*, C(2')); 110.57 (*dm*, C(5')); 113.06 (*dd*, C(8)); 116.96 (*m*, C(6')); 117.02 (*m*, C(6)); 119.94 (*q*, C(4a)); 125.81 (*m*, C(5) or C(7)); 127.16 (*m*, C(3)); 127.98 (*m*, C(3''), C(5'')); 128.71 (*m*, C(2''), C(4''), C(6'')); 129.19 (*m*, C(5) or C(7)); 135.26 (*s*, C(4)); 139.17 (*m*, C(1'')); 141.32 (*m*, C(1')); 143.08 (*t*, C(8a)); 147.65 (*m*, C(3')); 148.49 (*quint. m*, C(4')). MS: 357 (6, M^+), 343 (22), 342 (100), 326 (20), 220 (34).

(±)-2-(3,5-Difluorophenyl)-1,2-dihydro-2-methyl-4-phenylquinoline (**11**): Purified by FC (AcOEt/hexane 1:12) and recrystallization of the hydrochloride from Et_2O. Yellow resin. IR (KBr): 3387*m*, 3082*w*, 3055*w*, 2972*w*, 1599*s*, 1491*m*, 1470*s*, 1433*s*, 1317*m*, 1153*w*, 1117*s*, 986*s*, 854*s*, 770*s*, 750*s*, 702*s*. ^{1}H-NMR ($CDCl_3$): 1.76 (*s*, Me–C(2)); 4.19 (*s*, NH); 5.59 (*s*, H–C(3)); 6.61 (*m*, H–C(6), H–C(8)); 6.68 (*tt*, *J* = 8.0, 1.0, H–C(4')); 6.72 (*dd*, *J* = 8.0, 1.0, H–C(5)); 7.04–7.10 (*m*, H–C(2'), H–C(6'), H–C(5')); 7.32–7.42 (*m*, 5 arom. H). ^{13}C-NMR (^{1}H-coupled; $CDCl_3$): 30.12 (*qd*, Me–C(2)); 56.94 (*m*, C(2)); 102.09 (*dt*, C(4')); 108.41 (*dd*, C(2'), C(6')); 113.36 (*dd*, C(8)); 117.78 (*dd*, C(6)); 120.11 (*q*, C(4a)); 126.35 (*ddd*, C(5) or C(7)); 127.41 (*dq*, C(3)); 127.59 (*dt*, C(4'')); 128.23 (*dd*, C(3''), C(5'')); 128.90 (*dt*, C(2''), C(6'')); 129.23 (*ddd*, C(5) or C(7)); 136.64 (*s*, C(4)); 138.98 (*q*, C(1'')); 142.61 (*t*, C(8a)); 153.19 (*m*, C(1')); 163.03 (*dd*, C(3'), C(5')). MS: 333 (10, M^+), 319 (34), 318 (100), 220 (48), 204 (20), 178 (10), 159 (12), 148 (15).

(±)-1,2-Dihydro-2-methyl-2-(naphthalen-1-yl)-4-phenylquinoline (**12**): Purified by FC (AcOEt/hexane 1:7) and recrystallization of the free amine from AcOEt/hexane 1:3. Orange powder. M.p. 175–176°. IR (KBr): 3371*m*, 3053*w*, 3026*w*, 2982*w*, 1622*m*, 1597*m*, 1464*s*, 1313*m*, 1250*m*, 1090*m*, 924*w*, 798*w*, 781*s*, 766*m*, 702*s*. ^{1}H-NMR ($CDCl_3$): 2.10 (*s*, Me–C(2)); 4.18 (*s*, NH); 5.67 (*d*, *J* = 1.0, H–C(3)); 6.52 (*d*, *J* = 8.0, H–C(8)); 6.62 (*td*, *J* = 8.0, 1.0, H–C(6)); 7.03 (*d*, *J* = 8.0, H–C(5)); 7.07 (*td*, *J* = 8.0, 1.0, H–C(7)); 7.30–7.48 (*m*, 8 arom. H); 7.63 (*d*, *J* = 8.0, 1 arom. H); 7.82 (*d*, *J* = 8.0, 1 arom. H); 7.87 (*m*, 1 arom. H); 9.05 (*m*, 1 arom. H). ^{13}C-NMR (^{1}H-couplet; $CDCl_3$): 29.08 (*q*, Me–C(2)); 57.98 (*m*, C(2)); 113.47 (*dd*, C(8)); 117.09 (*dd*, C(6)); 119.80 (*quint.*, C(4a)); 123.35 (*dm*, arom. C); 124.42 (*dm*, arom. C); 125.03 (*m*, arom. C); 125.12 (*m*, arom. C); 126.33 (*m*, C(5) or C(7)); 127.26 (*m*, C(3)); 127.70 (*m*, arom. C); 128.12 (*m*, C(3''), C(5'')); 128.83 (*m*, arom. C); 128.88 (*m*, C(2''), C(6'')); 129.09 (*m*, C(5) or C(7)); 129.12 (*m*, arom. C); 129.99 (*m*, arom. C); 132.16 (*quint.*, C(8'a)); 135.09 (*m*, C(4'a)); 135.36 (*m*, C(4)); 139.42 (*q*, C(1'')); 141.80 (*s*, C(1')); 142.98 (*t*, C(8a)). MS: 347 (6, M^+), 333 (28), 220 (36), 204 (12).

(±)-2-(Furan-2-yl)-1,2-dihydro-2-methyl-4-phenylquinoline (**13**): Purified by recrystallization of the hydrochloride from acetone/Et_2O 1:1 and FC (AcOEt/hexane 1:7) of the free base. Brown powder. M.p. 84–86°. IR (KBr): 3368*s*, 3051*w*, 2976*w*, 2926*w*, 1628*m*, 1601*m*, 1499*m*, 1466*s*, 1450*m*, 1313*m*, 1151*m*, 1013*m*, 847*m*, 771*s*, 758*s*, 737*s*, 702*s*. ^{1}H-NMR ($CDCl_3$): 1.76 (*s*, Me–C(2)); 4.28 (*s*, NH); 5.63 (*s*, H–C(3)); 6.18 (*dd*, *J* = 4.0, 1.0, H–C(3')); 6.28 (*dd*, *J* = 4.0, 2.0, H–C(4')); 6.54 (*dd*, *J* = 8.0, 1.0, H–C(8)); 6.59 (*td*, *J* = 8.0, 1.0, H–C(6)); 6.92 (*dd*, *J* = 8.0, 1.0, H–C(5)); 7.02 (*td*, *J* = 8.0, 1.0, H–C(7)); 7.33–7.41 (*m*, 6 arom. H). ^{13}C-NMR (^{1}H-coupled; $CDCl_3$): 28.28 (*qd*, Me–C(2)); 53.85 (*m*, C(2)); 105.17 (*ddd*, C(3')); 110.15 (*ddd*, C(4')); 113.51 (*dd*, C(8)); 117.74 (*dd*, C(6)); 120.52 (*q*, C(4a)); 125.78 (*m*, C(5) or C(7)); 126.15 (*m*, C(4'')); 127.48 (*m*, C(3)); 128.18 (*m*, C(3''), C(5'')); 128.86 (*m*, C(5) or C(7)); 128.93 (*m*, C(2''), C(6'')); 137.37 (*s*, C(4)); 139.20 (*m*, C(1'')); 141.83 (*ddd*, C(5')); 143.0 (*t*, C(8a)); 159.18 (*m*, C(2')). MS: 287 (10, M^+), 273 (30), 272 (100), 243 (10).

(±)-6-Chloro-1,2-dihydro-2-methyl-2,4-diphenylquinoline (**14**): Purified by recrystallization of the hydrochloride from Et_2O and FC (AcOEt/hexane 1:7) of the free base. Brown resin. IR (KBr): 3391*m*, 3055*w*, 3024*w*, 2966*w*, 1597*m*, 1483*s*, 1443*s*, 1304*m*, 1256*m*, 1130*m*, 1028*m*, 808*s*, 775*s*, 762*s*, 700*s*. ^{1}H-NMR ($CDCl_3$): 1.78 (*s*, Me–C(2)); 4.21 (*s*, NH); 5.68 (*s*, H–C(3)); 6.49 (*d*, *J* = 8.0, H–C(8)); 6.87 (*d*, *J* = 2.0, H–C(5)); 6.98 (*dd*, *J* = 8.0, 2.0, H–C(7)); 7.23 (*tm*, *J* = 8.0, arom. H); 7.30–7.42 (*m*, 7 arom. H). ^{13}C-NMR (^{1}H-coupled; $CDCl_3$): 29.91 (*q*, Me–C(2)); 57.07 (*m*, C(2)); 114.18 (*d*, C(8)); 121.53 (*m*, C(4a) or C(6)); 121.69 (*m*, C(4a) or C(6)); 125.18 (*dt*, C(2'), C(6')); 125.61 (*dd*, C(5) or C(7)); 126.92 (*m*, C(3)); 127.61 (*dt*, C(4')); 128.32 (*m*, C(3'), C(5')); 128.40 (*m*, C(3''), C(5'')); 128.47 (*m*, C(4'')); 128.76 (*dt*, C(2''), C(6'')); 130.07 (*dm*, C(5) or C(7)); 134.81 (*s*, C(4)); 138.57 (*q*, C(1'')); 141.68 (*t*, C(8a)); 148.21 (*s*, C(1')). MS: 331 (6, M^+(^{35}Cl)), 318 (36), 316 (100), 254 (28), 203 (10), 141 (10).

(±)-6-Chloro-2-(4-chlorophenyl)-1,2-dihydro-2-methyl-4-phenylquinoline (**15**): Purified by FC (AcOEt/hexane 1:9) and recrystallization of the hydrochloride from Et_2O/EtOH 2:1. Yellow crystals. M.p. 119–121°. IR (KBr): 3366*m*, 3057*w*, 2968*w*, 1597*w*, 1483*s*, 1443*s*, 1300*m*, 1092*s*, 1011*s*, 829*m*, 810*m*, 777*m*, 760*m*, 702*s*. ^{1}H-NMR ($CDCl_3$): 1.75 (*s*, Me–C(2)); 4.18 (*s*, NH); 5.62 (*s*, H–C(3)); 6.49 (*d*, *J* = 8.0, H–C(8)); 6.87 (*d*, *J* = 2.0, H–C(5)); 6.98 (*dd*, *J* = 8.0, 2.0, H–C(7)); 7.29–7.34 (*m*, 4 arom. H); 7.35–7.41 (*m*, 3 arom. H); 7.48 (*dm*, *J* = 8.0, H–C(3'), H–C(5')). ^{13}C-NMR (^{1}H-coupled; $CDCl_3$): 29.80 (*qd*, Me–C(2)); 56.76 (*m*, C(2)); 114.29 (*d*, C(8)); 121.51 (*t*, C(4a)); 121.97 (*td*, C(6)); 125.71 (*dd*, C(5) or C(7)); 126.69 (*dd*, C(2'), C(6')); 127.74 (*dt*, C(4'')); 128.38 (*m*, C(3'), C(5')); 128.47 (*m*, C(3''), C(5'')); 128.62 (*m*, C(3)); 128.72 (*m*, C(2''), C(6'')); 129.47 (*dm*, C(5) or C(7)); 132.71 (*tt*, C(4')); 135.17 (*m*, C(4)); 138.35 (*q*, C(1'')); 141.43 (*t*, C(8a)); 146.76 (*m*, C(1')). MS: 365 (8, M^+(^{35}Cl)), 352 (64), 350 (100), 256 (10), 254 (30), 203 (12), 139 (12).

(±)-6-Chloro-1,2-dihydro-2-(4-hydroxyphenyl)-2-methyl-4-phenylquinoline (**16**): Purified by recrystallization of the hydrochloride from EtOH. Yellow amorphous solid. M.p. 53–55°. IR (KBr): 3383*m*, 3055*m*, 3024*w*, 2970*w*, 1705*m*, 1597*s*, 1510*s*, 1483*s*, 1466*m*, 1256*m*, 1175*m*, 831*s*, 810*s*, 770*s*, 731*m*, 700*s*. ^{1}H-NMR ($CDCl_3$): 1.73 (*s*, Me–C(2)); 5.61 (*s*, H–C(3)); 6.44 (*d*, *J* = 8.0, H–C(8)); 6.78 (*d*, *J* = 8.0, H–C(3′), H–C(5′)); 6.86 (*d*, *J* = 3.0, H–C(5)); 6.96 (*d*, *J* = 3.0, H–C(5)); 7.30–7.42 (*m*, 7 arom. H). ^{13}C-NMR (^{1}H-coupled; $CDCl_3$): 29.72 (*qd*, Me–C(2)); 56.64 (*m*, C(2)); 114.30 (*d*, C(8)); 115.36 (*dd*, C(3′), C(5′)); 121.59 (*m*, C(4a) or C(6)); 121.70 (*m*, C(4a) or C(6)); 125.57 (*m*, C(5) or C(7)); 126.75 (*m*, C(2′), C(6′)); 127.67 (*m*, C(4″)); 128.39 (*m*, C(3″), C(5″)); 128.46 (*m*, C(3)); 128.79 (*m*, C(2″), C(6″)); 130.45 (*m*, C(5) or C(7)); 134.59 (*s*, C(4)); 138.62 (*q*, C(1″)); 140.29 (*m*, C(1′)); 141.67 (*t*, C(8a)); 154.89 (*tt*, C(4′)). MS: 347 (10, M^+(^{35}Cl)), 334 (44), 332 (100), 254 (30), 203 (16), 149 (15), 139 (10).

(±)-6-Chloro-1,2-dihydro-2-methyl-2-(4-nitrophenyl)-4-phenylquinoline (**17**): Purified by recrystallization of the hydrochloride from AcOEt. Orange powder. M.p. 68–70°. IR (KBr): 3371*m*, 3074*w*, 2974*w*, 1597*m*, 1516*s*, 1485*s*, 1352*s*, 1258*w*, 858*m*, 850*m*, 810*m*, 773*m*, 754*m*, 700*s*. ^{1}H-NMR ($CDCl_3$): 1.82 (*s*, Me–C(2)); 4.30 (*s*, NH); 5.68 (*s*, H–C(3)); 6.57 (*d*, *J* = 8.0, H–C(8)); 6.87 (*d*, *J* = 2.0, H–C(5)); 7.02 (*dd*, *J* = 8.0, 2.0, H–C(7)); 7.30 (*dm*, *J* = 8.0, H–C(3″), H–C(5″)); 7.38–7.43 (*m*, H–C(2″), H–C(4″), H–C(6″)); 7.69 (*dm*, *J* = 8.0, H–C(2′), H–C(6′)); 8.19 (*dm*, *J* = 8.0, H–C(3′), H–C(5′)). ^{13}C-NMR (^{1}H-coupled; $CDCl_3$): 30.03 (*qd*, Me–C(2)); 57.28 (*m*, C(2)); 114.67 (*d*, C(8)); 121.74 (*t*, C(4a)); 122.75 (*m*, C(6)); 123.81 (*m*, C(3′), C(5′)); 126.07 (*m*, C(7)); 126.21 (*m*, C(2′), C(6′)); 128.06 (*m*, C(3)); 128.37 (*m*, C(4″)); 128.54 (*m*, C(3″), C(5″)); 128.78 (*m*, C(2″), C(6″)); 129.02 (*dd*, C(5)); 136.28 (*m*, C(4)); 138.13 (*m*, C(1″)); 141.11 (*t*, C(8a)); 146.79 (*m*, C(4′)); 155.36 (*m*, C(1′)). MS: 376 (10, M^+), 363 (46), 361 (100), 315 (42), 256 (18), 254 (53), 140 (14), 139 (18).

(±)-6-Chloro-1,2-dihydro-2-(4-methoxyphenyl)-2-methyl-4-phenylquinoline (**18**): Purified by FC (AcOEt/hexane 1:9). Yellow resin. IR (KBr): 3387*m*, 3055*w*, 3024*w*, 2961*w*, 2928*w*, 1599*m*, 1510*s*, 1483*s*, 1464*s*, 1443*s*, 1304*m*, 1250*s*, 1178*s*, 1030*m*, 829*s*, 804*s*, 768*s*, 701*s*. ^{1}H-NMR ($CDCl_3$): 1.76 (*s*, Me–C(2)); 3.80 (*s*, MeO–C(4′)); 4.17 (*s*, NH); 5.62 (*s*, H–C(3)); 6.47 (*d*, *J* = 8.0, H–C(8)); 6.88 (*m*, H–C(5)); 6.88 (*m*, H–C(5), H–C(3′), H–C(5′)); 7.32–7.42 (*m*, 5 arom. H); 7.44 (*m*, H–C(2′), H–C(6′)). ^{13}C-NMR (^{1}H-coupled; $CDCl_3$): 29.79 (*q*, Me–C(2)); 55.15 (*q*, MeO–C(4′)); 56.64 (*m*, C(2)); 113.67 (*dd*, C(2′), C(5′)); 114.14 (*d*, C(8)); 121.49 (*m*, C(4a) or C(6)); 121.60 (*m*, C(4a) or C(6)); 125.55 (*dd*, C(5) or C(7)); 126.48 (*dd*, C(2′), C(6′)); 127.59 (*dt*, C(4″)); 128.83 (*dd*, C(3″), C(5″)); 128.42 (*dd*, C(3)); 128.78 (*dd*, C(2″), C(6″)); 130.33 (*dm*, C(5) or C(7)); 134.56 (*s*, C(4)); 138.64 (*q*, C(1″)); 140.55 (*m*, C(1′)); 141.68 (*m*, C(8a)); 158.44 (*m*, C(4′)). MS: 361 (6, M^+(^{35}Cl)), 348 (32), 346 (100), 254 (20).

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