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A Novel Reductive Cyclization of *o*-Nitrobenzamides and Ketones Promoted by Low-valent Titanium Reagent

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A short and facile synthesis of a series of 1,2-dihydroquiazolin-4(3*H*)-ones was accomplished in good yields via novel reductive cyclization of *o*-nitrobenzamides with ketones promoted by $TiCl_4$/Zn system. The structure was established on the basis of elemental analysis, IR, ^{1}H NMR and confirmed by a single-crystal X-ray diffraction analysis. This method has the advantages of easily accessible starting materials, convenient manipulation and moderate to high yields.

Keywords quinazolin-4(3*H*)-one, low-valent titanium, *o*-nitrobenzamide

Introduction

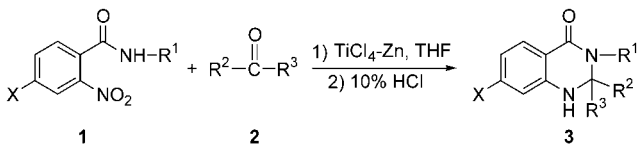
Low-valent titanium reagents have an exceedingly high ability to promote reductive coupling of carbonyl compounds and are attracting increasing interest in organic synthesis. Many other functional groups can also be coupled by these reagents.[1] Recently, we have reported the cyclodimerization of *α*,*β*-unsaturated ketone and *α*,*β*-unsaturated nitrile compounds promoted by this reagent, leading to the formation of functional cyclopentanes[2] and cyclopentenes[3] respectively.

Preparations of quinazolin-4(3*H*)-ones are in demand because of their potential biological and pharmaceutical activities.[4] Unfortunately, synthetic methods for the elaboration of this bicyclic system of rather simple structure are not general, and often involve low-yielding multistep reaction sequences. The main synthetic approaches to such compounds include preliminary amidation of 2-aminobenzonitrile, 2-aminobenzoic acid or ethyl 2-aminobenzoate[5] and the aza-Wittig reactions of *α*-azido-substituted aromatic imides.[6] One-pot synthesis of this type of compounds has been described, however, the condensation of 2-aminobenzoic acid with amides or nitriles must be carried out either at high temperature or in a sealed tube at 200 ℃.[7] Here we wish to describe a new method for the preparation of 1,2-dihydroquinazolin-4(3*H*)-ones promoted by the $TiCl_4$/Zn system using *o*-nitrobenzamides as the starting material.

Results and discussion

When *o*-nitrobenzamides **1** and ketones **2** were treated with low-valent titanium, prepared from titanium tetrahchloride and Zn powder in anhydrous THF, the intermolecular reductive cyclization product 1,2-dihydroquinazolin-4(3*H*)-ones **3** were obtained in good yields (Scheme 1). The results are summarized in Table 1.

Scheme 1



1 2 3

Table 1 Synthesis of 1,2-dihydroquinazolin-4(3*H*)-ones promoted by $TiCl_4$/Zn

Entry	Compound	X	R^1	R^2	R^3	Isolated yield/%
1	**3a**	H	4-$CH_3C_6H_4$	CH_3	CH_3	88
2	**3b**	H	4-ClC_6H_4	CH_3	CH_3	71
3	**3c**	H	4-BrC_6H_4	CH_3	CH_3	83
4	**3d**	H	3-Cl-4-FC_6H_3	CH_3	CH_3	77
5	**3e**	Cl	C_6H_5	CH_3	CH_3	85
6	**3f**	Cl	4-$CH_3C_6H_4$	CH_3	CH_3	89
7	**3g**	Cl	4-ClC_6H_4	CH_3	CH_3	86
8	**3h**	Cl	4-BrC_6H_4	CH_3	CH_3	87
9	**3i**	Cl	3-Cl-4-FC_6H_3	CH_3	CH_3	74
10	**3j**	H	H	CH_3	CH_3	88
11	**3k**	H	H	CH_3	C_2H_5	79
12	**3l**	H	H	C_2H_5	C_2H_5	86
13	**3m**	Cl	H	CH_3	CH_3	80
14	**3n**	Cl	H	CH_3	C_2H_5	74
15	**3o**	Cl	H	C_2H_5	C_2H_5	71

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The reaction of *o*-nitrobenzamide **1** and cyclic ketone **4** with the same reagent afforded 2,2-polymethylene-1,2-dihydroquinazolin-4(3*H*)-ones **5** (Scheme 2) and the results are summarized in Table 2. However, *o*-nitrobenzamide failed to react with acetophenone or 1-tetralone under the same reaction conditions.

Scheme 2

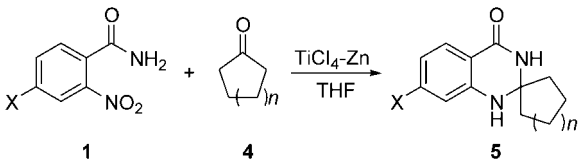

Table 2 Reductive cyclization of *o*-nitrobenzamides and cyclic ketones

Entry	Compound	X	*n*	Isolated yield/%
1	**5a**	H	1	84
2	**5b**	H	2	63
3	**5c**	Cl	1	89
4	**5d**	Cl	2	83

The structures of **3** and **5** were confirmed by IR, ^{1}H NMR and elemental analysis. Among them, **3a** was further confirmed by X-ray analysis (Figure 1).

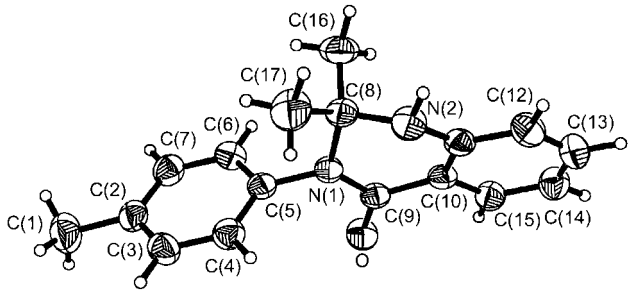

Figure 1 ORTEP diagram of **3a**.

In summary, a series of 1,2-dihydroquinazolin-4(3*H*)-ones was synthesized via reductive cyclization of *o*-nitrobenzamides with ketones promoted by the $TiCl_4$/Zn system. The advantages of our method are easily accessible starting materials, convenient manipulation and moderate to high yields.

Experimental

General

Tetrahydrofuran was distilled from sodium-benzophenone immediately prior to use. All reactions were conducted under a nitrogen atmosphere. Melting points are uncorrected. Infrared spectra were recorded on an FTIR-8101 spectrometer in KBr. ^{1}H NMR spectra were determined on an Inova-400 MHz spectrometer in $CDCl_3$ solution. Chemical shifts are expressed in ppm downfield from internal tetramethylsilane. Microanalysis was carried out on a Perkin-Elmer 2400 II instrument. X-ray diffraction was recorded on a Siemens P4 diffractometer.

General procedure for the synthesis of 1,2-dihydroquinazolin-4(3*H*)-ones

$TiCl_4$ (2.2 mL, 20 mmol) was added dropwise using a syringe to a stirred suspension of zinc dust (2.6 g, 40 mmol) in freshly distilled anhydrous THF (20 mL) at room temperature under a dry nitrogen atmosphere. After completion of the addition, the mixture was refluxed for 2 h. The suspension of the low-valent titanium reagent formed was cooled to room temperature and a solution of 2-nitrobenzamide (5 mmol) and ketone (5 mmol) in THF (15 mL) was added dropwise. The mixture was stirred at room temperature under a dry nitrogen atmosphere until the reaction was complete (the reaction was monitored by TLC). The reaction mixture was quenched with 10% HCl (50 mL) and extracted with $ClCH_2CH_2Cl$ (3×50 mL). The combined extracts were washed with water (3×50 mL) and dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the crude products **3** or **5** were purified by recrystallization from 95% ethanol.

2,2-Dimethyl-3-(4-methylphenyl)-1,2-dihydroquinazolin-4(3*H*)-one (**3a**) m.p. 255—256 ℃; ^{1}H NMR ($CDCl_3$) δ: 1.49 (s, 6H, 2×CH_3), 2.38 (s, 3H, CH_3), 6.67 (d, J=8.8 Hz, 1H, C8-H), 6.87 (dd, J_1=8.4 Hz, J_2=7.2 Hz, 1H, C6-H), 7.12 (d, J=8.4 Hz, 2H, C2'-H, C6'-H), 7.23 (d, J=8.4 Hz, 2H, C3'-H, C5'-H), 7.32 (dd, J_1=8.8 Hz, J_2=7.2 Hz, 1H, C7-H), 7.95 (d, J=8.4 Hz, 1H, C5-H); IR (KBr) ν: 3305, 2973, 1627, 1575, 1519, 1489, 1464, 1433, 1399, 1378, 1277, 1225, 1175, 1107, 1022, 947, 813, 784, 755, 718, 697 cm^{-1}. Anal. calcd for $C_{17}H_{18}N_2O$: C 76.66, H 6.81, N 10.52; found C 76.83, H 6.59, N 10.63.

2,2-Dimethyl-3-(4-chlorophenyl)-1,2-dihydroquinazolin-4(3*H*)-one (**3b**) m.p. 275—276 ℃; ^{1}H NMR ($CDCl_3$) δ: 1.50 (s, 6H, 2×CH_3), 6.69 (d, J=8.4 Hz, 1H, C8-H), 6.89 (dd, J_1=7.2 Hz, J_2=8.0 Hz, 1H, C6-H), 7.19 (d, J=8.4 Hz, 2H, C2'-H, C6'-H), 7.35 (dd, J_1=8.4 Hz, J_2=8.0 Hz, 1H, C7-H), 7.41 (d, J=8.4 Hz, 2H, C3'-H, C5'-H), 7.94 (d, J=7.2 Hz, 1H, C5-H); IR (KBr) ν: 3307, 2972, 1628, 1518, 1489, 1465, 1433, 1398, 1377, 1338, 1273, 1179, 1088, 1016, 872, 818, 756, 727, 696 cm^{-1}. Anal. calcd for $C_{16}H_{15}ClN_2O$: C 67.02, H 5.27, N 9.77; found C 67.18, H 5.03, N 9.83.

2,2-Dimethyl-3-(4-bromophenyl)-1,2-dihydroquinazolin-4(3*H*)-one (**3c**) m.p. 264—265 ℃; ^{1}H NMR ($CDCl_3$) δ: 1.49 (s, 6H, 2×CH_3), 6.68 (d, J=8.0 Hz, 1H, C8-H), 6.88 (dd, J_1=8.0 Hz, J_2=7.2 Hz, 1H, C6-H), 7.13 (d, J=8.0 Hz, 2H, C2'-H, C6'-H), 7.34 (dd, J_1=8.0 Hz, J_2=7.2 Hz, 1H, C7-H), 7.13 (d, J=8.4 Hz, 2H, C3'-H, C5'-H), 7.94 (d, J=8.0 Hz, 1H, C5-H); IR (KBr) ν: 3307, 2968, 1627, 1579, 1489, 1465, 1433, 1397, 1377, 1271, 1171, 1098, 1067, 1012, 871, 815, 756, 696 cm^{-1}. Anal. calcd for $C_{16}H_{15}BrN_2O$: C 58.02, H 4.56, N 8.46; found C 58.18, H 4.54, N 8.65.

2,2-Dimethyl-3-(3-choloro-4-fluorolphenyl)-1,2-dihydroquinazolin-4(3*H*)-one (**3d**) m.p. 228—229

℃; ^{1}H NMR ($CDCl_3$) δ: 1.50 (s, 6H, 2×CH_3), 6.68 (d, J=8.8 Hz, 1H, C8-H), 6.89 (dd, J_1=7.2 Hz, J_2=8.0 Hz, 1H, C6-H), 7.12—7.15 (m, 1H, C6'-H), 7.21 (dd, J_1=8.0 Hz, J_2=8.8 Hz, 1H, C7-H), 7.31—7.37 (m, 2H, C2'-H, C5'-H), 7.935 (d, J=7.2 Hz, 1H, C5-H); IR (KBr) v: 3292, 2974, 1636, 1492, 1467, 1436, 1390, 1371, 1333, 1279, 1256, 1214, 1175, 1118, 1062, 1025, 930, 915, 876, 856, 819, 804, 746, 717, 694 cm^{-1}. Anal. calcd for $C_{16}H_{14}ClFN_2O$: C 63.06, H 4.63, N 9.19; found C 63.14, H 4.51, N 9.30.

7-Chloro-2,2-dimethyl-3-phenyl-1,2-dihydroquinazolin-4(3*H*)-one (**3e**) m.p. 270—272 ℃; ^{1}H NMR ($CDCl_3$) δ: 1.49 (s, 6H, 2×CH_3), 6.68 (s, 1H, C8-H), 6.83 (d, J=8.4 Hz, 1H, C6-H), 7.22—7.55 (m, 5H, ArH), 7.87 (d, J=8.4 Hz, 1H, C5-H); IR (KBr) v: 3286, 2968, 1628, 1606, 1516, 1488, 1454, 1411, 1389, 1371, 1279, 1224, 1178, 1077, 1032, 1002, 988, 950, 931, 898, 850, 809, 758, 733, 699 cm^{-1}. Anal. calcd for $C_{16}H_{15}ClN_2O$: C 67.02, H 5.27, N 9.77; found C 67.25, H 5.18, N 9.69.

7-Chloro-2,2-dimethyl-3-(4-methylphenyl)-1,2-dihydroquinazolin-4(3*H*)-one (**3f**) m.p. 270—272 ℃; ^{1}H NMR ($CDCl_3$) δ: 1.49 (s, 6H, 2×CH_3), 2.38 (s, 3H, CH_3), 6.67 (s, 1H, C8-H), 6.82 (d, J=8.0 Hz, 1H, C6-H), 7.10 (d, J=7.2 Hz, 2H, C2'-H, C6'-H), 7.23 (d, J=7.2 Hz, 2H, C3'-H, C5'-H), 7.87 (d, J=8.0 Hz, 1H, C5-H); IR (KBr) v: 3300, 2971, 1633, 1510, 1484, 1457, 1413, 1366, 1284, 1258, 1175, 1106, 1077, 1025, 992, 901, 849, 811, 786, 765, 709, 693 cm^{-1}. Anal. calcd for $C_{17}H_{17}ClN_2O$: C 67.88, H 5.70, N 9.31; found C 67.93, H 5.54, N 9.49.

7-Chloro-2,2-dimethyl-3-(4-chlorolphenyl)-1,2-dihydroquinazolin-4(3*H*)-one (**3g**) m.p. 268—269 ℃; ^{1}H NMR ($CDCl_3$) δ: 1.49 (s, 6H, 2×CH_3), 6.68 (s, 1H, C8-H), 6.84 (d, J=8.0 Hz, 1H, C6-H), 7.17 (d, J=8.4 Hz, 2H, C2'-H, C6'-H), 7.50 (d, J=8.4 Hz, 2H, C3'-H, C5'-H), 7.86 (d, J=8.0 Hz, 1H, C5-H); IR (KBr) v: 3310, 2969, 1629, 1612, 1510, 1491, 1455, 1408, 1389, 1369, 1328, 1281, 1258, 1173, 1079, 1024, 990, 902, 848, 813,743, 698 cm^{-1}. Anal. calcd for $C_{16}H_{14}Cl_2N_2O$: C 59.83, H 4.39, N 8.72; found C 60.04, H 4.21, N 8.81.

7-Chloro-2,2-dimethyl-3-(4-bromolphenyl)-1,2-dihydroquinazolin-4(3*H*)-one (**3h**) m.p. 270—272 ℃; ^{1}H NMR ($CDCl_3$) δ: 1.49 (s, 6H, 2×CH_3), 6.69 (s, 1H, C8-H), 6.84 (d, J=8.0 Hz, 1H, C6-H), 7.11 (d, J=8.0 Hz, 2H, C2'-H, C6'-H), 7.57 (d, J=8.0 Hz, 2H, C3'-H, C5'-H), 7.86 (d, J=8.0 Hz, 1H, C5-H); IR (KBr) v: 3297, 2965, 1625, 1515, 1486, 1455, 1409, 1372, 1279, 1174, 1097, 1068, 1023, 1010, 903, 856, 814, 768, 715, 695 cm^{-1}. Anal. calcd for $C_{16}H_{14}BrClN_2O$: C 52.56, H 3.86, N 7.66; found C 52.68, H 3.74, N 7.54.

7-Chloro-2,2-dimethyl-3-(3-choloro-4-fluorolphenyl)-1,2-dihydroquinazolin-4(3*H*)-one (**3i**) m.p. 273—274 ℃; ^{1}H NMR ($CDCl_3$) δ: 1.50 (s, 6H, 2×CH_3), 6.69 (s, 1H, C8-H), 6.85 (d, J=8.0 Hz, 1H, C6-H), 7.11—7.15 (m, 1H, C6'-H), 7.30—7.37 (m, 2H, C2'-H, C5'-H), 7.85 (d, J=8.0 Hz, 1H, C5-H); IR (KBr) v: 3302, 2970, 1636, 1606, 1495, 1456, 1412, 1366, 1281, 1256, 1210, 1178, 1152, 1124, 1078, 1060, 1028, 989, 949, 891, 873, 763, 729, 712, 694 cm^{-1}. Anal. calcd for $C_{16}H_{13}Cl_2FN_2O$: C 56.66, H 3.86, N 8.26; found C 56.81, H 3.72, N 8.44.

2,2-Dimethyl-1,2-dihydroquinazolin-4(3*H*)-one (**3j**) m.p. 185—186 ℃; ^{1}H NMR ($CDCl_3$) δ: 1.57 (s, 6H, 2×CH_3), 6.30 (s, 1H, NH), 6.63 (d, J=8.0 Hz, 1H, C8-H), 6.83 (dd, J_1=8.0 Hz, J_2=6.8 Hz, 1H, C6-H), 7.31 (dd, J_1=8.0 Hz, J_2=6.8 Hz, 1H, C7-H), 7.89 (d, J=8.0 Hz, 1H, C5-H); IR (KBr) v: 3260, 3180, 2968, 1634, 1608, 1520, 1486, 1424, 1392, 1362, 1334, 1279, 1182, 753 cm^{-1}. Anal. calcd for $C_{10}H_{12}N_2O$: C 68.16, H 6.86, N 15.90; found C 68.30, H 6.63, N 15.73.

2-Methyl-2-ethyl-1,2-dihydroquinazolin-4(3*H*)-one (**3k**) m.p. 184—185 ℃; ^{1}H NMR ($CDCl_3$) δ: 0.99 (t, J=8.0 Hz, 3H, CH_3), 1.50 (s, 3H, CH_3), 1.81 (q, J=8.0 Hz, 2H, CH_2), 6.16 (s, 1H, NH), 6.62 (d, J=8.0 Hz, 1H, C8-H), 6.81 (dd, J_1=8.0 Hz, J_2=7.2 Hz, 1H, C6-H), 7.30 (dd, J_1=8.0 Hz, J_2=7.2 Hz, 1H, C7-H), 7.87 (d, J=8.0 Hz, 1H, C5-H); IR (KBr) v: 3279, 3178, 2974, 1643, 1609, 1512, 1489, 1430, 1395, 1331, 1275, 1182, 1153, 758 cm^{-1}. Anal. calcd for $C_{11}H_{14}N_2O$: C 69.45, H 7.42, N 14.73; found C 69.61, H 7.38, N 14.54.

2,2-Diethyl-1,2-dihydroquinazolin-4(3*H*)-one (**3l**) m.p. 190—191 ℃; ^{1}H NMR ($CDCl_3$) δ: 0.97 (t, J=8.0 Hz, 6H, 2×CH_3), 1,76 (q, J=8.0 Hz, 4H, 2×CH_2), 5.98 (s, 1H, NH), 6.60 (d, J=8.0 Hz, 1H, C8-H), 6.78 (dd, J_1=8.0 Hz, J_2=8.0 Hz, 1H, C6-H), 7.28 (dd, J_1=8.0 Hz, J_2=8.0 Hz, 1H, C7-H), 7.85 (d, J=8.0 Hz, 1H, C5-H); IR (KBr) v: 3320, 3175, 2974, 1646, 1607, 1510, 1489, 1463, 1429, 1395, 1329, 1274, 1150, 758 cm^{-1}. Anal. calcd for $C_{12}H_{16}N_2O$: C 70.56, H 7.90, N 13.71; found C 70.81, H 7.68, N 13.59.

7-Chloro-2,2-dimethyl-1,2-dihydroquinazolin-4(3*H*)-one (**3m**) m.p. 243—244 ℃; ^{1}H NMR ($CDCl_3$) δ: 1.58 (s, 6H, 2×CH_3), 6.21 (s, 1H, NH), 6.64 (s, 1H, C8-H), 6.80 (d, J=8.8 Hz, 1H, C6-H), 7.81 (d, J=8.8 Hz, 1H, C5-H); IR (KBr) v: 3291, 3178, 2975, 1643, 1607, 1510, 1480, 1458, 1416, 1387, 1363, 1276, 1244, 1178, 1078, 984, 857, 777 cm^{-1}. Anal. calcd for $C_{10}H_{11}ClN_2O$: C 57.01, H 5.26, N 13.30; found C 57.27, H 5.14, N 13.18.

7-Chloro-2-methyl-2-ethyl-1,2-dihydroquinazolin-4(3*H*)-one (**3n**) m.p. 173—174 ℃; ^{1}H NMR ($CDCl_3$) δ: 0.98 (t, J=8.0 Hz, 3H, CH_3), 1.50 (s, 3H, CH_3), 1.79 (q, J=8.0 Hz, 2H, CH_2), 6.29 (s, 1H, C8-H), 6.75 (d, J=8.0 Hz, 1H, C6-H), 6.96 (s, 1H, NH), 7.78 (d, J=8.0 Hz, 1H, C5-H); IR (KBr) v: 3304, 3191, 2974, 1642, 1608, 1510, 1480, 1454, 1419, 1320, 1276, 1156, 1079, 896, 854, 778 cm^{-1}. Anal. calcd for $C_{11}H_{13}ClN_2O$: C 58.80, H 5.83, N 12.47; found C 58.94, H 5.62, N 12.33.

7-Chloro-2,2-diethyl-1,2-dihydroquinazolin-4(3*H*)-one (**3o**) m.p. 164—166 ℃; ^{1}H NMR ($CDCl_3$) δ: 0.96 (t, J=8.0 Hz, 6H, 2×CH_3), 1.75 (q, J=8.0 Hz, 4H, 2×CH_2), 6.59 (s, 1H, NH), 6.61 (s, 1H, C8-H), 6.71 (d, J=8.0 Hz, 1H, C6-H), 7.76 (d, J=8.0 Hz, 1H, C5-H); IR (KBr) v: 3286, 3215, 2967, 1644, 1608, 1513, 1483, 1461, 1420, 1363, 1324, 1276, 1175, 1155, 1082, 986,

912, 874, 774 cm^{-1}. Anal. calcd for $C_{12}H_{15}ClN_2O$: C 60.38, H 6.33, N 11.74; found C 60.56, H 6.18, N 11.59.

2,2-Tetramethylene-1,2-dihydroquinazolin-4(3*H*)-one (**5a**) m.p. 251—253 ℃; ^1H NMR ($CDCl_3$) δ: 1.79—1.80 (m, 4H, CH_2CH_2), 1.88—1.97 (m, 4H, 2×CH_2), 6.17 (s, 1H, NH), 6.65 (d, J=8.0 Hz, 1H, C8-H), 6.85 (dd, J_1=7.2 Hz, J_2=7.2 Hz, 1H, C6-H), 7.31 (dd, J_1=7.2 Hz, J_2=8.4 Hz, 1H, C7-H), 7.88 (d, J=7.2 Hz, 1H, C6-H); IR (KBr) v: 3292, 3159, 2972, 1638, 1606, 1517, 1485, 1431, 1385, 1334, 1270, 1149, 1088, 1049, 954, 849, 803, 781, 753 cm^{-1}. Anal. calcd for $C_{12}H_{14}N_2O$: C 71.26, H 6.98, N 13.85; found C 71.38, H 6.71, N 14.02.

2,2-Pentamethylene-1,2-dihydroquinazolin-4(3*H*)-one (**5b**) m.p. 224—225 ℃; ^1H NMR ($CDCl_3$) δ: 1.47—1.48 (m, 2H, CH_2), 1.53—1.60 (m, 4H, 2×CH_2), 1.80—1.84 (m, 4H, 2×CH_2), 6.19 (s, 1H, NH), 6.65 (d, J=8.4 Hz, 1H, C8-H), 6.82 (dd, J_1=7.6 Hz, J_2=7.2 Hz, 1H, C6-H), 7.30 (dd, J_1=8.4 Hz, J_2=7.2 Hz, 1H, C7-H), 7.87 (d, J=8.0 Hz, 1H, C5-H); IR (KBr) v: 3367, 3170, 2923, 1651, 1612, 1507, 1484, 1417, 1382, 1323, 1269, 1210, 1178, 1145, 1093, 1040, 1004, 951, 914, 855, 802, 760 cm^{-1}. Anal. calcd for $C_{13}H_{16}N_2O$: C 72.19, H 7.46, N 12.95; found C 72.32, H 7.28, N 13.15.

7-Chloro-2,2-tetramethylene-1,2-dihydroquinazolin-4(3*H*)-one (**5c**) m.p. 223—225 ℃; ^1H NMR ($CDCl_3$) δ: 1.62—1.80 (m, 4H, 2×CH_2), 1.81—1.96 (m, 4H, 2×CH_2), 6.23 (s, 1H, NH), 6.65 (s, 1H, C8-H), 6.80 (d, J=8.8 Hz, 1H, C6-H), 7.80 (d, J=8.8 Hz, 1H, C5-H); IR (KBr) v: 3260, 3189, 1650, 1608, 1519, 1480, 1421, 1361, 1318, 1277, 1154, 1078, 1044, 936, 899, 855, 768 cm^{-1}. Anal. calcd for $C_{12}H_{13}ClN_2O$: C 60. 98, H 5.54, N11.84; found C 61.02, H 5.36, N 11.97.

7-Chloro-2,2-pentamethylene-1,2-dihydroquinazolin-4(3*H*)-one (**5d**) m.p. 221—222 ℃; ^1H NMR ($CDCl_3$) δ: 1.45—1.49 (m, 2H, CH_2), 1.53.—1.67 (m, 4H, 2×CH_2), 1.78—1.83 (m, 4H, 2×CH_2), 6.17 (s, 1H, NH), 6.66 (s, 1H, C8-H), 6.77 (d, J=8.8 Hz, 1H, C6-H), 7.79 (d, J=8.8 Hz, 1H, C5-H); IR (KBr) v: 3362, 3249, 1699, 1600, 1576, 1507, 1464, 1336, 1152, 1044, 890, 751 cm^{-1}. Anal. calcd for $C_{13}H_{15}ClN_2O$: C 62.28, H 6.03, N 11.17; found C 62.43, H 5.96, N 11.33.

Crystal data and structure refinement for 3a

Crystals suitable for X-ray analysis were obtained by slow evaporation of an ethanol solution of **3a**. Crystal data: $C_{17}H_{18}N_2O$, M_r=266.33, monoclinic, space group $P2(1)/n$, a = 1.1917(2) nm, b = 0.6911(1) nm, c = 1.7821(4) nm, β=98.81(1)°, V=1.4504(5) nm^3, Z=4, D_c=1.220 $g\cdot cm^{-3}$, $F(000)$=568, μ(Mo Kα)=0.077 mm^{-1}, colorless block crystals, crystal size 0.56 mm× 0.52 mm×0.32 mm. Intensity data were collected at 295 K on a Siemens P4 diffractometer with graphite-monochromated Mo Kα radiation (λ=0.071073 nm): 2706 independent reflections were collected using ω scan mode in the range of $1.93°<\theta<25.50°$, of which 1628 intensity data with [$I>2\sigma(I)$] were observed. The corrections for Lp factors were applied. The structure was solved by direct methods and expanded using Fourier techniques. Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms were induced in F value calculation but fixed during the structure refinement. A full matrix least-squares refinement gave final R=0.0433 and wR =0.0851 with $w=1/[\sigma^2F_o^2+(0.0643P)^2]$, S=0.921. The maximum peak in the final difference Fourier map is 136 e/nm^3 and the minimum peak is −136 e/nm^3. In the final circle refinement the largest parameter shift $(\Delta/\sigma)_{max}$ is 0.000.

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