Synthetic Applications of Bis(iminophosphoranes) – Preparation of Some Derivatives of the 11*H*-Quinazolino[2,3-*b*]- and Quinazolino[4,3-*b*]quinazoline Ring Systems

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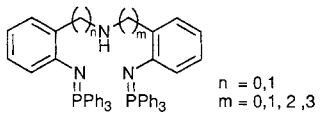
Received June 7, 1996

Keywords: Bis(iminophosphoranes) / Guanidines, bicyclic / Aza Wittig reaction

Aza Wittig reaction of bis(iminophosphorane) **3** with two equivalents of aryl isocyanates directly provided the bicyclic guanidines **4**. However, **3** undergoes intramolecular aza Wittig reaction on thermal treatment to give the iminophosphorane **6** derived from the 2-(*o*-azidophenyl)-4(3*H*)-quinazolinone. Compound **6** reacts with isocyanates, acyl chlorides and carbon disulfide to yield quinazolino[4,3-*b*]quinazoline derivatives **8a–c**, **9a–c**, **10**, and **11**.

In recent years iminophosphoranes have been increasingly used as valuable synthetic intermediates[1]. In particular, iminophosphoranes are versatile building blocks for the construction of azaheterocycles which constitute the backbone of various biologically active compounds[2]. However, the chemistry of bis(iminophosphoranes) has been studied less extensively. Bis(iminophosphoranes) have been shown to have synthetic potential as a result of their ability to react with reagents bearing two functionalities or with two separate reagents with the same or different functionality[3]. In this context, we have reported that *C,C'*-bis(iminophosphoranes) of type **1** react with aryl isocyanates or isothiocyanates to give rigid [5 + 5]-, [5 + 6]-, [6 + 6]-, [6 + 7]-, [6 + 8]-bicyclic and [5 + 6 + 6]-tricyclic guanidines[4].



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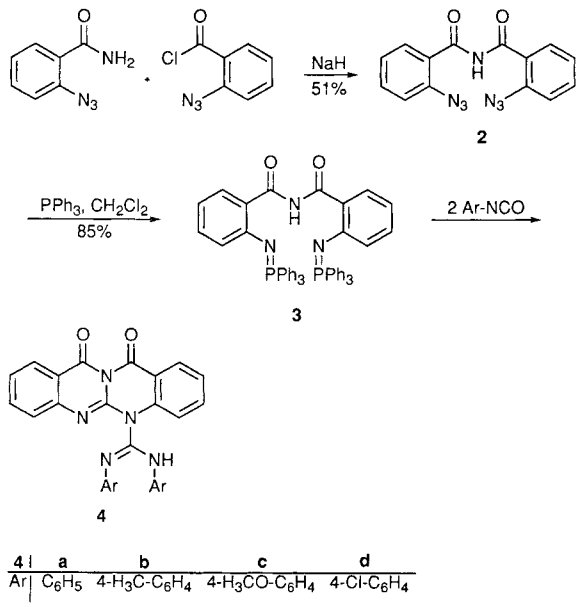
As a further employment of this type of *C,C'*-bis(iminophosphoranes), we studied the preparation and characterization of the chemical behavior of the related *C,C'*-bis(iminophosphorane) **3**, in which the two methylene groups (n = m = 1) of the tether connecting the two aromatic rings are replaced by two carbonyl groups. At first it was of interest to see if the bis(iminophosphorane) **3** shows the same behavior as observed for bis(iminophosphorane) **1** (n = m = 1) with respect to aryl isocyanates.

The required bis(iminophosphorane) **3** was easily prepared by acylation of *o*-azidobenzamide with *o*-azidobenzoyl chloride to bis-azide **2** (51%) and Staudinger reaction of the resulting bisazide with triphenylphosphane (85%). Aza Wittig-type reaction of bis(iminophosphorane) **3** with two equivalents of aryl isocyanates in dichloromethane at room temperature gave directly 11*H*-quinazolino[2,3-*b*]quinazoline-11,13-(5*H*)-diones **4**, bearing two guanidine-type moieties, in modest yields (20–33%) (Scheme 1). The ^{1}H- and ^{13}C-NMR spectra of compounds **4** indicate that the two aryl groups are nonequivalent. Several derivatives of this ring system[5] display sedative properties[6].

Scheme 1



As no phosphorus-containing intermediates were detected when the reaction was monitored by ^{31}P-NMR spectroscopy, the conversion **3** → **4** could probably involve two initial aza Wittig-type reactions between the two iminophosphorane moieties and the two equivalents of isocyanate to give the bis(carbodiimides) **5** which provides the final products **4** (Scheme 2).

When bis(iminophosphorane) **3** was heated in dry toluene at reflux temperature the iminophosphorane **6** was obtained in 65% yield. This conversion involves an intramolecular aza Wittig reaction where an amido carbonyl group acts as the carbonyl partner[7]. Iminophosphorane **6** reacts with alkyl and aryl isocyanates in dry dichloromethane at

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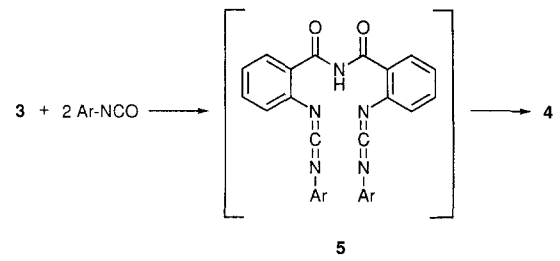
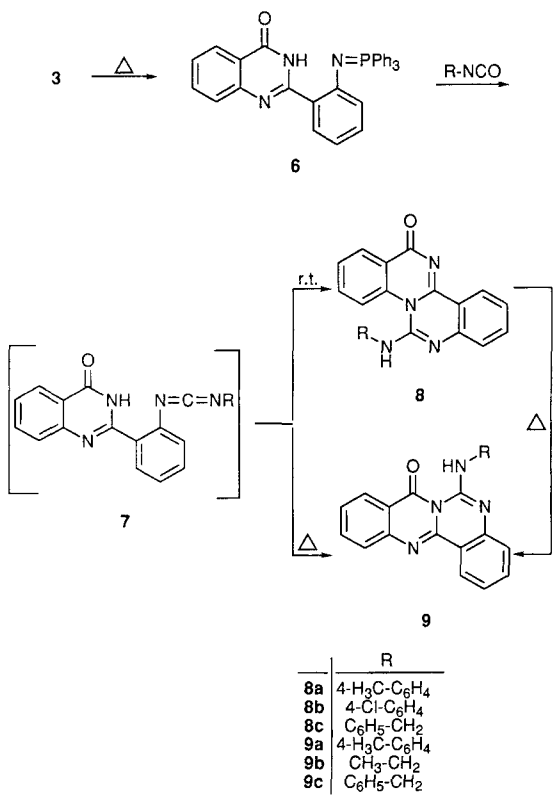
Scheme 2



room temperature to give the tetracyclic 13*H*-quinazolino[3,4-*a*]quinazolin-13-ones **8** in yields ranging from 50 to 70%. However, when the reaction was carried out in toluene at reflux temperature the isomeric 8*H*-quinazolino[4,3-*b*]quinazolin-8-ones **9** were isolated as the sole products in 42–73% yields. Compounds **8** were converted in almost quantitative yields into the isomeric compounds **9** by heating in toluene at reflux temperature. A closely related intramolecular rearrangement in the 4-quinazolinone series is reported in ref.[8].

Scheme 3



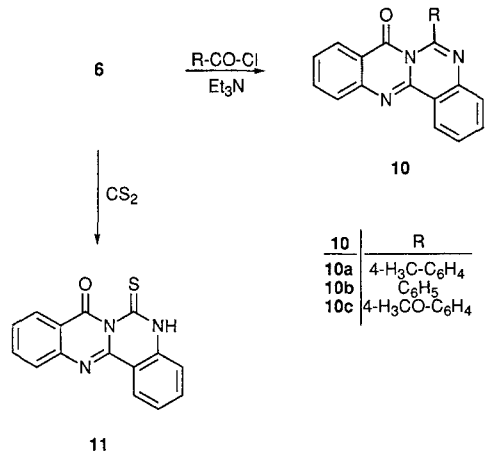
	R
8a	4-H_3C-C_6H_4
8b	4-Cl-C_6H_4
8c	C_6H_5-CH_2
9a	4-H_3C-C_6H_4
9b	CH_3-CH_2
9c	C_6H_5-CH_2

The structure of compounds **8** and **9** were assigned on the basis of the spectroscopic data. In particular, the IR spectra of compounds **8** show an amidic carbonyl stretching band in the region $\tilde{\nu}$ = 1687–1679 cm^{-1}, while those of compounds **9** exhibit a band for the carbonyl group in the region $\tilde{\nu}$ = 1648–1646 cm^{-1} due to the effect of the conjugated carbon-nitrogen double bond[9].

These conversions can be viewed as an initial aza Wittig reaction affording the intermediate carbodiimide **7** which undergoes cyclization either at room temperature in 1-position of the quinazolinone system to give **8a–c** or at reflux temperature in 3-position to give the most thermally stable structure **9**[8].

Iminophosphorane **6** also react with acyl chlorides in the presence of triethylamine in toluene at reflux temperature to give 6-substituted quinazolino[4,3-*b*]quinazolin-8-ones **10** in modest yields (29–35%). Spectroscopic data of compounds **10** are similar to those of compounds **9**. The reaction of iminophosphorane **6** with carbon disulfide in a sealed tube at 160°C provided **11** in excellent yield (92%).

Scheme 4



10	R
10a	4-H_3C-C_6H_4
10b	C_6H_5
10c	4-H_3CO-C_6H_4

We gratefully acknowledge the financial support of the *Dirección General de Investigación Científica y Técnica* (project number PB92-0984). One of us (C. C.) also thanks to the *Ministerio de Educación y Ciencia* for a scholarship.

Experimental Section

Melting points are uncorrected: Kofler hot-stage apparatus. – IR: Nicolet FT 5DX; nujol emulsions between NaCl plates. – ^1H and ^{13}C NMR: Bruker AC 200. – MS (70 eV): Hewlett-Packard 5993C, EI. – CC: Silica gel 60 (Merck) as stationary phase; columns of 4.5 cm diameter and 70 cm height.

Bis(iminophosphorane) **3**: To a solution of *N*-(*o*-azidobenzoyl)-*o*-azidobenzamide (1.53 g, 5 mmol) in dry dichloromethane (25 ml), a solution of triphenylphosphane (2.60 g, 10 mmol) in the same solvent (30 ml) was added dropwise at 0°C under N_2. The reaction mixture was stirred for 1 h, then allowed to warm at room temp. and stirring was continued for 11 h. The solvent was removed under reduced pressure and the residue was recrystallized from diethyl ether to give **3**: Yield 3.53 g (91%), m.p. 234–235°C, colorless prisms. – IR: $\tilde{\nu}$ = 3200, 1708, 1589, 1476, 1436, 1335, 1278, 1108, 1011, 998, 752, 724, 701 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 13.74 (s, NH, 1H), 8.01 (dt, ^3J = 7.7 Hz, ^4J = 2.2 Hz, 2H, 6-H), 7.47 (ddd, ^3J_P = 12.1 Hz, ^3J = 8.3 Hz, ^4J = 1.3 Hz, 12H, 2'-H), 7.31 (td, ^3J = 7.2 Hz, ^4J = 1.3 Hz, 6H, 4'-H), 7.02 (ddd, ^3J = 8.3 Hz, ^3J = 7.2 Hz, ^4J_P = 2.9 Hz, 12H, 3'-H), 6.86 (td, ^3J = 7.7 Hz, ^4J = 1.9 Hz, 2H, 5-H), 6.74 (td, ^3J = 8.0 Hz, ^4J = 2.2 Hz, 2H, 4-H), 6.22 (d, ^3J = 8.0 Hz, 2H, 3-H). – ^{13}C NMR ($CDCl_3$): δ = 167.0 (CO), 150.3 (d, ^2J_P = 1.5 Hz, C-2), 132.5 (C-6)*, 132.1 (d, ^2J_P = 10.0 Hz, *o*-C), 131.5 (d, ^4J_P = 3.0 Hz, *p*-C), 131.3 (C-4)*, 129.7 (d, ^1J_P =

99.5 Hz, *i*-C), 128.6 (d, ^3J_P = 12.0 Hz, *m*-C), 127.9 (d, ^3J_P = 22.9 Hz, C-1), 122.7 (^3J_P = 13.0 Hz, C-3), 116.9 (C-5). – ^{31}P NMR ($CDCl_3$): d = 7.3. – MS; *m/z* (%): 497 (18), 277 (100), 183 (96). – $C_{50}H_{39}N_3O_2P_2$ (775.8): calcd. C 77.41, H 5.07, N 5.42; found C 77.80, H 4.99, N 5.39.

Preparation of Guanidines **4**. – *General Procedure:* To a solution of the bis(iminophosphorane) **2** (0.50 g, 0.64 mmol) in dry dichloromethane (20 ml), the appropriate isocyanate (1.28 mmol) was added. The reaction mixture was stirred at room temp. under N_2 for 24 h. The solution was filtered and the filtrate was concentrated to dryness. The crude product was chromatographed on a silica gel column with ethyl acetate/hexane as eluent (1:1) to give **4**.

4a: (Ar = C_6H_5): Yield 0.05 g (18%), m.p. 192–194°C, colorless prisms. – IR: $\tilde{\nu}$ = 3294, 1704, 1681, 1666, 1592, 1547, 1452, 1352, 1258, 1133, 771, 692 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 8.40 (br. s, NH, 1H), 7.71 (d, ^3J = 7.7 Hz, 2H), 7.62 (d, ^3J = 6.9 Hz, 2H), 7.45–7.33 (m, 4H), 7.27–7.17 (m, 4H), 7.13–6.99 (m, 3H), 6.92–6.86 (m, 2H), 6.57 (t, ^3J = 7.5 Hz, 1H). – ^{13}C NMR ($CDCl_3$): δ = 168.3 (CO), 160.5 (CO), 146.0 (q), 144.6 (q), 144.0 (q), 138.5 (q), 138.0 (q, × 2), 135.2, 132.0, 129.5, 129.0 (2 × CH), 128.7, 128.4, 128.0, 127.8, 126.9 (q), 125.9, 124.4, 124.1, 122.8, 120.2, 119.4 (q). – MS; *m/z* (%): 457 (6) [M$^+$], 236 (47), 221 (77), 195 (100). – $C_{28}H_{19}N_5O_2$ (457.5): calcd. C 73.51, H 4.19, N 15.31; found C 73.68, H 4.23, N 15.50.

4b: (Ar = 4-CH_3–C_6H_4): Yield 0.10 g (33%), m.p. 199–200°C, colorless prisms. – IR: $\tilde{\nu}$ = 3266, 1689, 1671, 1659, 1589, 1350, 1257, 1193, 1129, 912, 814, 770, 704 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 8.28 (br. s, NH, 1H), 7.66 (d, ^3J = 8.3 Hz, 2H), 7.58 (d, ^3J = 8.2 Hz, 2H), 7.44–7.09 (m, 9H), 6.99–6.91 (m, 2H), 6.68 (t, ^3J = 7.3 Hz, 1H), 2.36 (s, CH_3, 3H), 2.33 (s, CH_3, 3H). – ^{13}C NMR ($CDCl_3$): δ = 168.4 (CO), 160.5 (CO), 146.1 (q), 144.8 (q), 144.2 (q), 138.9 (q), 138.1 (q), 136.0 (q), 135.4 (q), 135.1, 134.0 (q), 131.8, 130.1, 129.5, 128.7, 128.2, 127.9, 127.8, 127.1 (q), 126.0, 123.9, 122.8, 120.4, 119.4 (q), 21.2 (CH_3), 21.9 (CH_3). – MS; *m/z* (%): 485 (3) [M$^+$], 250 (100), 209 (34). – $C_{30}H_{23}N_5O_2$ (485.5): calcd. C 74.21, H 4.77, N 14.42; found C 73.89, H 4.80, N 14.37.

4c: (Ar = 4-CH_3O–C_6H_4): Yield 0.10 g (29%), m.p. 162–163°C, colorless prisms. – IR: $\tilde{\nu}$ = 3300, 1700, 1681, 1660, 1594, 1507, 1462, 1356, 1249, 1169, 1030, 829, 769 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 8.36 (br. s, NH, 1H), 7.71 (d, ^3J = 8.8 Hz, 2H), 7.62 (d, ^3J = 8.7 Hz, 2H), 7.44–7.31 (m, 2H), 7.25–7.08 (m, 3H), 7.02–6.95 (m, 3H), 6.91–6.83 (m, 3H), 6.70 (t, ^3J = 7.5 Hz, 1H), 3.81 (s, O-CH_3, 3H), 3.79 (s, O-CH_3, 3H). – ^{13}C NMR ($CDCl_3$): δ = 168.6 (CO), 160.6 (CO), 159.8 (q), 156.5 (q), 146.1 (q), 144.8 (q), 144.3 (q), 138.2 (q), 135.1, 131.9, 131.2 (q), 131.2 (q), 129.7, 128.7, 127.9, 127.8, 127.1 (q), 125.9, 123.9, 122.8, 121.9, 119.4 (q), 114.7, 114.2, 55.5 (OCH_3), 55.5 (OCH_3). – MS; *m/z* (%): 517 (2) [M$^+$], 267 (49), 108 (100). – $C_{30}H_{23}N_5O_4$ (517.5): calcd. C 69.62, H 4.48, N 13.53; found C 70.00, H 4.52, N 13.43.

4d: (Ar = 4-Cl–C_6H_4): Yield 0.06 g (19%), m.p. 192–194°C, colorless prisms. – IR: $\tilde{\nu}$ = 3308, 1703, 1686, 1674, 1595, 1543, 1350, 1255, 1225, 1093, 839, 768 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 8.30 (br. s, NH, 1H), 7.68 (d, ^3J = 8.8 Hz, 2H), 7.57 (d, ^3J = 8.7 Hz, 2H), 7.50–7.40 (m, 4H), 7.34–7.21 (m, 5H), 7.04–6.94 (m, 2H), 6.88 (ddd, ^3J = 8.2 Hz, ^3J = 7.1 Hz, ^4J = 1.0 Hz, 1H). – ^{13}C NMR ($CDCl_3$): δ = 168.1 (CO), 160.5 (CO), 146.1 (q), 144.2 (q), 143.7 (q), 137.6 (q), 136.9 (q), 136.5 (q), 135.6, 134.7 (q), 132.3, 129.7, 129.6 (q), 129.2, 129.0, 128.8, 128.2, 128.0, 126.4 (q), 126.0, 124.5, 122.7, 120.9, 119.4 (q). – MS; *m/z* (%): 528 (6) [M$^+$ + 2], 527 (18), 526 (12) [M$^+$], 525 (22), 257 (19), 255 (57), 90 (100). – $C_{28}H_{17}Cl_2N_5O_2$ (526.4): calcd. C 63.89, H 3.26, N 13.30; found C 64.22, H 3.25, N 13.23.

Iminophosphorane **6**: A solution of **3** (7.7 g, 0.99 mmol) in dry toluene (300 ml) was heated at reflux temperature for 24 h. After cooling, the solvent was removed under reduced pressure and the residual material was chromatographed on a silica gel column with ethyl acetate/hexane (1:1) as eluent to give **6**. Yield 3.2 g (65%), m.p. 178–180°C, colorless prisms. – IR: $\tilde{\nu}$ = 3431, 1666, 1602, 1579, 1558, 1476, 1441, 1328, 1271, 1112, 1013, 999, 695 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 12.86 (s, NH, 1H), 8.71 (d, ^3J = 8.1 Hz, 1H), 8.29 (d, ^3J = 8.1 Hz, 1H), 7.80 (ddd, ^3J_P = 12.3 Hz, ^3J = 8.1 Hz, ^4J = 1.5 Hz, 6H), 7.61–7.53 (m, 11H), 7.37 (td, ^3J = 7.3 Hz, ^4J = 1.5 Hz, 1H), 6.95 (td, ^3J = 7.3 Hz, ^4J = 1.8 Hz, 1H), 6.82 (td, ^3J = 7.5 Hz, ^4J = 1.5 Hz, 1H), 6.52 (d, ^3J = 8.1 Hz, 1H). – ^{13}C NMR ($CDCl_3$): δ = 162.5 (C-4), 154.6 (C-2), 150.9 (d, ^2J_P = 3.4 Hz, C-2′), 150.2 (C-8a), 133.7 (C-7), 132.6 (d, ^2J_P = 10.0 Hz, *o*-C), 132.5 (d, ^4J_P = 2.5 Hz, *p*-C), 131.3 (C-4′), 130.5 (d, ^2J_P = 2.1 Hz, C-6′), 129.1 (d, ^3J = 12.5 Hz, *m*-C), 128.7 (d, ^1J_P = 99.5 Hz, *i*-C), 127.4 (C-5), 126.2 (C-6), 125.0 (C-8), 123.0 (d, ^3J_P = 12.4 Hz, C-3′), 122.0 (d, ^3J_P = 19.0 Hz, C-1′), 121.4 (C-4a), 118.2 (C-5′). – ^{31}P NMR ($CDCl_3$): δ = 12.8. – MS; *m/z* (%): 498 (34), 497 (100) [M$^+$], 183 (14). – $C_{32}H_{24}N_3OP$ (497.5): calcd. C 77.25, H 4.86, N 8.45; found C 76.99, H 4.85, N 8.33.

Reaction of Iminophosphorane **6** *with Isocyanates:* To a solution of 2-[2-(triphenylphosphoranylideneamino)phenyl]-4(3*H*)-quinazolinone **6** (0.5 g, 1 mmol) in dry dichloromethane (20 ml) the corresponding isocyanate (1 mmol) was added. The mixture was stirred at room temp. for 24 h. The solvent was removed under reduced pressure and the crude product was chromatographed on a silica gel column with ethyl acetate/hexane (1:1) as eluent to give the corresponding 6-alkyl(aryl)amine-13*H*-quinazolino[3,4-*a*]quinazolin-13-one **8**.

8a: (R = 4-CH_3–C_6H_4): Yield 0.23 g (65%), m.p. 215–216°C, colourless needles. – IR: $\tilde{\nu}$ = 3261, 1648, 1627, 1600, 1527, 1509, 1457, 1343, 1316, 1270, 1241, 821, 763, 713 cm^{-1}. – MS; *m/z* (%): 353 (15) [M$^+$ + 1], 352 (68) [M$^+$], 351 (100). – $C_{22}H_{16}N_4O$ (352.4): calcd. C 74.98, H 4.58, N 15.90; found C 75.20, H 4.46, N 16.10.

8b: (R = 4-Cl-C_6H_4): Yield 0.26 g (70%), m.p. 192–193°C, yellow needles. – IR: $\tilde{\nu}$ = 3265, 1647, 1626, 1613, 1594, 1512, 1486, 1456, 1377, 1342, 1237, 823, 764 cm^{-1}. – MS; *m/z* (%): 374 (34) [M$^+$ + 2], 373 (60), 372 (92) [M$^+$], 371 (100). – $C_{21}H_{13}ClN_4O$ (372.8): calcd. C 67.66, H 3.51, N 15.03; found C 67.99, H 3.50, N 14.87.

8c: (R = C_6H_5–CH_2): Yield 0.18 g (50%), m.p. 200–202°C, yellow needles. – IR: $\tilde{\nu}$ = 3241, 1646, 1639, 1618, 1596, 1570, 1530, 1334, 1291, 1244, 1136, 1055, 1031, 967, 889, 872, 812, 769, 726, 700 cm^{-1}. – MS; *m/z* (%): 353 (8) [M$^+$ + 1], 352 (32) [M$^+$], 91 (100). – $C_{22}H_{16}N_4O$ (352.4): calcd. C 74.98, H 4.58, N 15.90; found C 75.12, H 4.51, N 15.78.

Preparation of 6-[Alkyl(aryl)amine]quinazolino[4,3-b]quinazolin-8-ones **9**. – *Method A:* To a solution of 2-[2-(triphenylphosphoranylideneamino)phenyl]-4(3*H*)-quinazolinone **6** (0.5 g, 1 mmol) in dry dichloromethane (20 ml) the corresponding isocyanate (1 mmol) was added. The resultant mixture was heated at reflux temperature for 3 h. After cooling, the solvent was removed under reduced pressure and the crude material was chromatographed on a silica gel column with ethyl acetate/hexane (1:1) as eluent to give **9**.

Method B: A solution of the corresponding 13*H*-quinazolino[3,4-*a*]quinazolin-13-one **8** (1 mmol) in dry toluene (20 ml) was heated at reflux temperature for 2 h. After cooling, the solvent was removed and the crude product was recrystallized from hexane to give **9**.

9a: (R = CH_3–C_6H_5): Yield 0.26 g (73%), m.p. 183–184°C, yellow needles. – IR: $\tilde{\nu}$ = 3264, 1687, 1632, 1596, 1553, 1467, 1377,

1341, 1280, 1130, 1090, 1022, 816, 765, 756, 714 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 12.13 (s, NH, 1H), 8.53 (dd, ^3J = 8.1 Hz, ^4J = 1.2 Hz, 1H), 8.27 (dd, ^3J = 8.1 Hz, ^4J = 1.2 Hz, 1H), 7.77 (ddd, ^3J = 8.1 Hz, ^3J = 6.9 Hz, ^4J = 1.2 Hz, 1H), 7.71–7.65 (m, 3H), 7.50 (ddd, ^3J = 8.2 Hz, ^3J = 7.2 Hz, ^4J = 1.2 Hz, 1H), 7.41 (ddd, ^3J = 8.1 Hz, ^3J = 6.9 Hz, ^4J = 1.2 Hz, 1H), 7.31 (dd, ^3J = 8.1 Hz, ^4J = 0.9 Hz, 1H), 7.19 (ddd, ^3J = 8.1 Hz, ^3J = 7.2 Hz, ^4J = 0.9 Hz, 1H), 7.14 (d, ^3J = 8.4 Hz, 2H), 2.33 (s, CH_3, 3H). – ^{13}C NMR ($CDCl_3$): δ = 164.5 (CO), 146.6 (q), 146.5 (q), 144.0 (q), 143.6 (q), 135.8, 135.7 (q), 133.6, 133.5 (q), 129.3, 127.4, 127.1, 126.4, 126.3, 124.8, 123.99, 121.5, 119.6 (q), 118.1 (q), 20.9 (CH_3). – MS; *m/z* (%): 353 (15) [M^+ + 1], 352 (68) [M^+], 351 (100). – $C_{22}H_{16}N_4O$ (352.4): calcd. C 74.98, H 4.58, N 15.90; found C 75.22, H 4.56, N 16.00.

9b: (R = CH_3–CH_2): Yield 0.19 g (65%), m.p. 159–160 °C, yellow needles. – IR: ṽ = 3267, 1685, 1629, 1599, 1582, 1540, 1466, 1377, 1343, 722 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 9.73 (br. s, NH, 1H), 8.40 (dd, ^3J = 8.1 Hz, ^4J = 1.3 Hz, 1H), 8.13 (dd, ^3J = 8.1 Hz, ^4J = 1.0 Hz, 1H), 7.70–7.55 (m, 2H), 7.40 (ddd, ^3J = 8.1 Hz, ^3J = 7.0 Hz, ^4J = 1.3 Hz, 1H), 7.28 (ddd, ^3J = 8.1 Hz, ^3J = 6.8 Hz, ^4J = 1.4 Hz, 1H), 7.16 (dd, ^3J = 8.1 Hz, ^4J = 1.3 Hz, 1H), 7.04 (ddd, ^3J = 8.1 Hz, ^3J = 7.0 Hz, ^4J = 1.3 Hz, 1H), 3.56 (dq, ^3J = 7.2 Hz, ^3J = 4.9 Hz, CH_2, 2H), 1.26 (t, ^3J = 7.2 Hz, CH_3, 3H). – ^{13}C NMR ($CDCl_3$): δ = 164.2 (CO), 146.9 (q), 146.8 (q), 145.2 (q), 135.5, 133.6, 127.3, 127.0, 126.4, 126.0, 124.2, 123.0, 119.7 (q), 117.4 (q), 36.9 (CH_2), 14.2 (CH_2); signals of the quaternary carbon atoms C-6 and C-14 were not observed. – MS; *m/z* (%): 291 (19) [M^+ + 1], 290 (100) [M^+], 262 (42). – $C_{17}H_{14}N_4O$ (290.3): calcd. C 70.33, H 4.86, N 19.30; found C 70.01, H 4.90, N 19.22.

9c: (R = C_6H_5–CH_2): Yield 0.15 g (42%), m.p. 162–163 °C, yellow needles. – IR: ṽ = 3262, 1679, 1627, 1597, 1547, 1536, 1481, 1468, 1377, 1342, 1285, 1135, 1024, 762, 740, 712, 695, 679 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 10.22 (t, ^3J = 5.1 Hz, NH, 1H), 8.49 (dd, ^3J = 8.2 Hz, ^4J = 1.4 Hz, 1H), 8.20 (dd, ^3J = 8.5 Hz, ^4J = 1.2 Hz, 1H), 7.77–7.67 (m, 2H), 7.48–7.45 (m, 3H), 7.40–7.23 (m, 5H), 7.14 (ddd, ^3J = 8.2 Hz, ^3J = 6.9 Hz, ^4J = 1.2 Hz, 1H), 4.75 (d, ^3J = 5.1 Hz, CH_2, 2H). – ^{13}C NMR ($CDCl_3$): δ = 164.2 (CO), 146.8 (q), 146.7 (q), 144.9 (q), 138.2 (q), 135.6, 133.6, 128.6, 128.0, 127.4, 127.3, 127.0, 126.5, 126.1, 124.4, 123.3, 119.6 (q), 117.6 (q), 46.1 (CH_2). – MS; *m/z* (%): 353 (10) [M^+ + 1], 352 (44) [M^+], 91 (100). – $C_{22}H_{16}N_4O$ (352.4): calcd. C 74.98, H 4.58, N 15.90; found C 75.12, H 4.60, N 16.00.

6-Arylquinazolino[4,3-b]quinazolin-8-ones **10**: A mixture of 2-[2-(triphenylphosphoranylideneamino)phenyl]-4(3*H*)-quinazolinone **6** (0.2 g, 0.5 mmol), the corresponding acyl chloride (0.5 mmol), triethylamine (0.05 g, 0.5 mmol), and dry toluene (8 ml) was stirred at reflux temperature for 24 h. After cooling, the precipitated ammonium salt was separated by filtration and the filtrate was concentrated to dryness. The residue was chromatographed on a silica gel column with ethyl acetate/hexane (1:2) to give **10**.

10a: (R = 4-CH_3–C_6H_4): Yield 0.04 g (35%), m.p. 176–178 °C, colorless prisms. – IR: ṽ = 1700, 1621, 1597, 1556, 1249, 1079, 764 cm^{-1}. – ^1H NMR ([D_6]DMSO): δ = 8.63 (d, ^3J = 7.8 Hz, 1H), 8.24 (d, ^3J = 7.8 Hz, 1H), 7.92 (t, ^3J = 7.8 Hz, 1H), 7.84–7.77 (m, 2H), 7.67–7.53 (m, 3H), 2.98 (s, CH_3, 3H). – ^{13}C NMR ([D_6]DMSO): δ = 160.8 (CO), 150.4 (q), 146.1 (q), 141.9 (q), 135.5, 133.6, 128.3 (q), 127.9, 127.1, 126.7, 126.6, 126.3, 125.1, 121.3 (q), 120.6 (q), 27.0 (CH_3). – MS; *m/z* (%): 261 (65) [M^+], 260 (100). – $C_{16}H_{11}N_3O$ (261.3): calcd. C 73.55, H 4.24, N 16.08; found C 73.77, H 4.21, N 15.97.

10b: (R = C_6H_5): Yield 0.05 g (29%), m.p. 297–298 °C, colorless needles. – IR: ṽ = 1695, 1596, 1554, 1465, 1260, 1100, 1027, 806, 767 cm^{-1}. – ^1H NMR ([D_6]DMSO): δ = 8.74 (d, ^3J = 8.1 Hz, 1H), 8.11 (d, ^3J = 8.1 Hz, 1H), 7.96–7.80 (m, 4H), 7.70 (t, ^3J = 8.1 Hz, 1H), 7.63–7.60 (m, 3H), 7.47–7.44 (m, 3H). – MS; *m/z* (%): 324 (21) [M^+ + 1], 323 (100) [M^+], 294 (64). – $C_{21}H_{13}N_3O$ (323.4): calcd. C 78.00, H 4.05, N 13.00; found C 77.91, H 3.96, N 13.10.

10c: (R = 4-CH_3O–C_6H_4): Yield 0.06 g (33%), m.p. 275–277 °C, colorless needles. – IR: ṽ = 1692, 1596, 1461, 1346, 1260, 1253, 830, 763 cm^{-1}. – ^1H NMR ([D_6]DMSO): δ = 8.69 (dd, ^3J = 7.8 Hz, ^4J = 1.2 Hz, 1H), 8.10 (dd, ^3J = 7.8 Hz, ^4J = 1.2 Hz, 1H), 7.94 (ddd, ^3J = 8.2 Hz, ^3J = 6.7 Hz, ^4J = 1.4 Hz), 1H, 7.85–7.75 (m, 3H), 7.66 (ddd, ^3J = 8.2 Hz, ^3J = 6.7 Hz, ^4J = 1.4 Hz, 1H), 7.54–7.50 (m, 3H), 6.71 (d, ^3J = 8.8 Hz, 2H), 3.85 (s, OCH_3, 3H). – MS, *m/z* (%): 354 (28) [M^+ + 1], 353 (100) [M^+]. – $C_{22}H_{15}N_3O_2$ (353.4): calcd. C 74.78, H 4.28, N 11.89; found C 74.98, H 4.21, N 12.01.

6(5H)-Thioxoquinazolino[4,3-b]quinazolin-8-one **11**: A solution of 2-[2-(triphenylphosphoranylideneamino)phenyl]-4(3*H*)-quinazolinone **6** (0.5 g, 1 mmol), carbon disulfide (5 ml) and dry toluene (30 ml) was heated in a sealed tube at 160 °C for 24 h. After cooling the separated solid was collected by filtration and recrystallized from toluene to give **11**. Yield 0.26 g (92%), m.p. 157–159 °C, yellow needles. – IR: ṽ = 3320, 1723, 1623, 1684, 1534, 1249, 1171, 1103, 1053, 765, 745 cm^{-1}. – ^1H NMR ([D_6]DMSO): δ = 13.02 (sa, NH, 1H), 8.34 (d, ^3J = 6.6 Hz, 1H), 8.15 (d, ^3J = 6.6 Hz, 1H), 7.86 (t, ^3J = 6.6 Hz, 1H), 7.70–7.63 (m, 2H), 7.54 (t, ^3J = 6.6 Hz, 1H), 7.37–7.34 (m, 2H). – ^{13}C NMR ([D_6]DMSO): δ = 170.51 (q), 160.16 (q), 144.58 (q), 136.24 (q), 135.13, 133.76, 126.00, 126.79, 126.51, 126.19, 124.64, 121.10 (q), 116.99 (q), 115.25; the signal of one quaternary carbon atom was not observed. – MS; *m/z* (%): 279 (31) [M^+], 278 (84), 90 (100). – $C_{15}H_9N_3OS$ (279.3): calcd. C 64.50, H 3.25, N 15.04; found C 64.65, H 3.24, N 14.97.

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