New Efficient Synthesis of 1,2,4-Triazolo[5,1-b]quinazolin-9(3H)-ones via a Tandem Aza-Wittig/Heterocumulene-Mediated Annulation

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The carbodiimides **2**, obtained from aza-Wittig reactions of iminophosphorane **1** with aromatic isocyanates, react with hydrazine to give, selectively, the 3-amino-2-arylaminoquinazolin-4(3*H*)-ones **4**. Reaction of **4** with triphenylphosphane, hexachloroethane and triethylamine produces iminophosphoranes **5**. A tandem aza-Wittig reaction of iminophosphorane **5** with isocyanate or acyl chloride generates the 1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-ones **7** or **9**, respectively, in satisfactory yield. The aza-Wittig reaction of iminophosphorane **5** with CS_2 or CO_2 gives the 1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-ones **14** or **17**, respectively. Further S-alkylation of **14** produces the 2-alkylthio-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-one **15**.

Introduction

The synthesis of derivatives of quinazolinone has been the focus of great interest recently. This is due, in part, to the broad spectrum of biological properties of these compounds. Some of these activities include antimicrobial,[1,2] anti-inflammatory,[3,4] antifungal,[5−7] anticancer[8] and AMPA receptor antagonistic properties.[9,10] The range of biological activities and characteristic chemical structures have made synthetic studies of quinazolinones very attractive.

Heterocycles containing the 1,2,4-triazole nucleus also exhibit various biological activities, and several of them have been used as fungicidal, bactericidal, insecticidal, antitumor and anti-inflammatory agents.[11−17] The introduction of a triazole ring to the quinazolinone system is expected to influence the biological activities significantly. In fact, some 1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-ones have been reported to exhibit good antifungal, antihistaminic and antirheumatic activities.[18,19]

The methods described so far for the preparation of some representative derivatives of this ring system involve either reaction of anthranilic acid with 3-mercapto-*s*-triazoles[18] or cyclization of 3-amino-2-arylaminoquinazolin-4(3*H*)-ones with carboxylic acids, acyl chlorides or aldehydes.[20−22] However, these methods often require relatively harsh acid, dehydrating conditions or heating at high temperature. Until now, no general and simple approach to 2-amino-substituted 1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-ones, which are of considerable interest as potential biologically active compounds or pharmaceuticals, has been reported.

Over the past twenty years, the aza-Wittig reactions of iminophosphoranes have received increasing attention in view of their utility in the synthesis of nitrogen heterocyclic compounds.[23] Annelation of ring systems with N-heterocycles by means of an aza-Wittig reaction has been widely utilized because of the availability of functionalized iminophosphoranes. Consequently, the discovery of novel functionalized iminophosphoranes is important in this respect. Recently we have become interested in the synthesis of quinazolinones, thienopyrimidinones and imidazolinones by an aza-Wittig reaction, with the aim of evaluating their fungicidal activities.[24−30] Here we wish to report a fundamentally new approach to the synthesis of 1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-ones by tandem aza-Wittig/heterocumulene-mediated annulation of easily accessible *N*-(2-arylamino-3*H*-quinazolin-4-on-3-yl)iminotriphenylphosphorane with isocyanates, acyl chloride, CS_2 or CO_2.

Results and Discussion

Iminophosphorane **1** reacts with aromatic isocyanates to give carbodiimides **2**, which were allowed to react with hydrazine to give, selectively, the 2-arylamino-3-aminoquinazolin-4(3*H*)-ones **4** in 72−81% yield (Scheme 1). It is worth noting that the reaction between carbodiimides **2** and aliphatic primary amine gives mainly abnormal 2-alkylamino-3-arylquinazolin-4(3*H*)-ones; this might be due to the geometry of the guanidine intermediate.[28] The normal formation of **4** can be rationalized in terms of an initial nucleophilic addition of hydrazine to give the guanidine intermediate **3**, which cyclizes to give **4** across the strong nucleophilic hydrazine group rather than the arylamine one.

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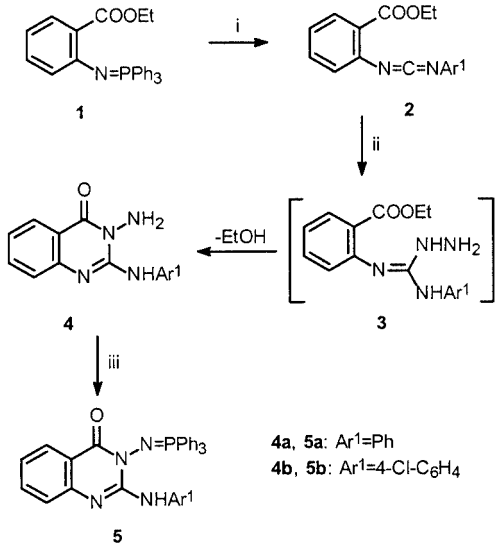
It has been reported that **4a** (Ar^1 = Ph) can be obtained by a rearrangement of hydrazine with 2-alkylthioquinazolin-4(3*H*)-one.[31a] The structure of **4** obtained by our new synthetic method was confirmed by comparison with the literature. Compounds **4** were easily converted into novel functionalized iminophosphoranes **5** upon reaction with triphenylphosphane, hexachloroethane and triethylamine in good yields (76−85%, Scheme 1).



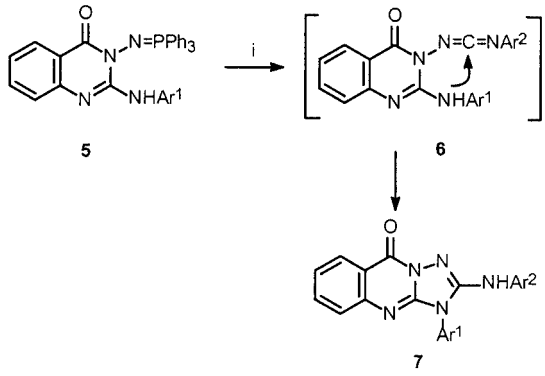
Scheme 1. Reaction conditions: (i) Ar^1NCO, CH_2Cl_2, 0−5 °C, 6−12 h; (ii) NH_2NH_2, EtOH, room temp., 10 min; (iii) PPh_3, C_2Cl_6, CH_2Cl_2, NEt_3, room temp., 4−6 h

When solutions of iminophosphoranes **5** in dry dichloromethane were treated with aromatic isocyanate at room temperature, the colour of the reaction mixture quickly turned red. This colour disappeared after a few minutes, and 2-arylamino-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-ones **7** were subsequently isolated as crystalline solids in excellent yields (86−94%, Table 1, Scheme 2). Presumably, the conversion of **5** into **7** involves initial aza-Wittig reaction between the iminophosphorane **5** and the isocyanate to give a carbodiimide **6** as a highly reactive intermediate, which easily undergoes ring closure across the arylamino group to give the otherwise not readily available 2-arylamino-substituted 1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-ones **7**. It is noteworthy that the reaction can be easily carried out at room temperature under mild neutral condition and the separation of **7** from the reaction mixture was also easily carried out by simple filtration.

Iminophosphoranes **5** react with acyl chlorides in the presence of triethylamine in dichloromethane at room temperature to give the 2-substituted 1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-ones **9** in good yield (63−88%, Table 2, Scheme 3). It is interesting to note that a similar iminophosphorane **10** reacts with acyl chloride at room temperature to give the corresponding *N*-acyl derivative **11**, which does not cyclize to give **12** even in refluxing toluene for 24 h or

Table 1. Preparation of 2-arylamino-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-ones **7**

Compd.	Ar^1	Ar^2	Yield (%)
7a	Ph	4-Me-C_6H_4	90
7b	Ph	3-Me-C_6H_4	90
7c	Ph	Ph	92
7d	Ph	4-Cl-C_6H_4	94
7e	Ph	3-Cl-C_6H_4	92
7f	4-Cl-C_6H_4	4-Me-C_6H_4	93
7g	4-Cl-C_6H_4	3-Me-C_6H_4	92
7h	4-Cl-C_6H_4	Ph	91
7i	4-Cl-C_6H_4	4-Cl-C_6H_4	87
7j	4-Cl-C_6H_4	3-Cl-C_6H_4	86

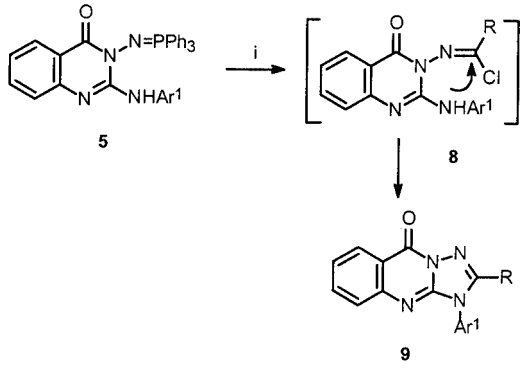


Scheme 2. Reaction conditions: (i) Ar^2NCO, CH_2Cl_2, room temp., 1−2 h

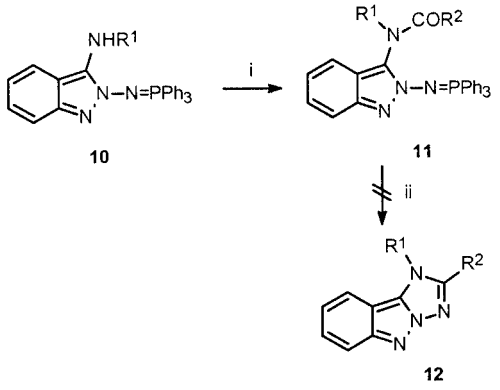
at temperatures slightly higher than its melting point (Scheme 4).[32] This unsuccessful cyclization by an intramolecular aza-Wittig reaction of **11** has been ascribed to the restricted conformation of the side chain at the 3-position, which could be entropically unfavourable for the cyclization. This phenomenon has also been found in other cases.[33−36] The easy transformation of **8** to **9** reveals the preferential reactivity of the iminophosphorane group of compound **5**, compared to the amino moiety, towards electrophilic reagents. Consequently, the formation of **9** can be viewed as an initial aza-Wittig reaction between the iminophosphorane **5** and acyl chloride in the presence of triethylamine, affording the intermediate imidoyl chloride **8**, which undergoes cyclization to give **9**.

Table 2. Preparation of 1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-ones **9**

Compd.	Ar^1	R	Yield (%)
9a	Ph	Me	73
9b	Ph	Ph	88
9c	Ph	4-Cl-C_6H_4	67
9d	Ph	$ClCH_2$	63
9e	Ph	4-Cl-$C_6H_4OCH_2$	78
9f	4-Cl-C_6H_4	Me	68
9g	4-Cl-C_6H_4	Ph	81
9h	4-Cl-C_6H_4	4-Cl-C_6H_4	73
9i	4-Cl-C_6H_4	$ClCH_2$	67



Scheme 3. Reaction conditions: (i) RCOCl, CH_2Cl_2, NEt_3, room temp., 2−4 h

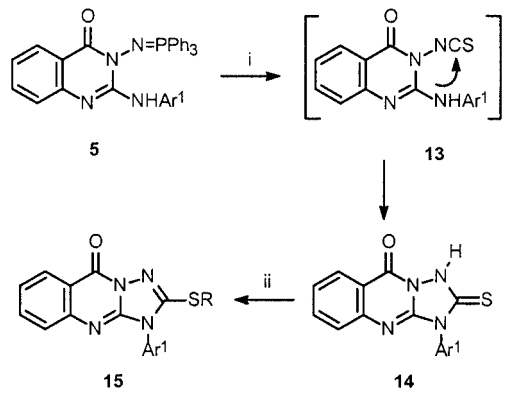


Scheme 4. Literature conditions for the reaction of iminophosphorane **10** with acyl chloride: (i) R^2COCl, THF, NEt_3, room temp.; (ii) toluene, reflux, 24 h or heating above the melting point

Iminophosphoranes **5** react with CS_2 in refluxing dichloromethane to give the 2-thioxo-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-ones **14** in good yield (83−87%, Scheme 5, Table 3). The formation of **14** can be viewed as an initial aza-Wittig reaction between the iminophosphorane **5** and CS_2 affording the intermediate isothiocyanate **13**, which undergoes cyclization to give **14**. *S*-Alkylation of **14** with alkyl halide in the presence of solid potassium carbonate gave the 2-alkylthio-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-ones **15** in satisfactory yields. With alkylating reagents such as RI and $BrCH_2COR$, the alkylation could be carried out at room temperature. With other reagents, the alkylation had to be carried out at 50 °C.

The 1,3-dihydro-1,2,4-triazolo[5,1-*b*]quinazolin-2,9-dione **17** was obtained in moderate yield (43%, Scheme 6) when iminophosphoranes **5** were allowed to react with CO_2 in dichloromethane. The formation of **17** can be viewed as an initial aza-Wittig reaction between the iminophosphorane **5** and CO_2, affording the intermediate isocyanate **16**, which undergoes cyclization to give **17**. The significantly low yield of the reaction might be due to the low solubility of CO_2 gas in the organic solvent.

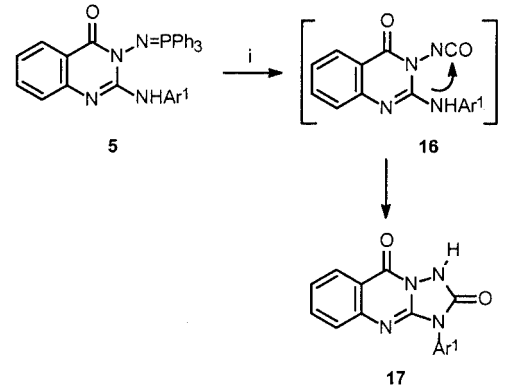
The structure of 1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-ones **7**, **9**, **14**, **15** and **17** was confirmed by their spectroscopic data. For example, the IR spectra of **7a** reveals N−H and C=O absorption bands at 3295 and 1675 cm^{-1}, respectively. The ^1H NMR spectrum of **7a** shows two singlets at δ = 6.12 and 2.33 ppm due to the NH and CH_3 groups, respectively. The signals attributable to the 8-H and other aromatic protons are found at δ = 8.44 and 7.17−7.72 ppm as a doublet and multiplets, respectively. The ^{13}C NMR



Scheme 5. Reaction conditions: (i) CS_2, CH_2Cl_2, 40 °C, 20 h; (ii) RX, CH_3CN, K_2CO_3 (s), room temp. or 50−60 °C, 1−4 h

Table 3. Composition of compounds **14**, **15** and **17**

Compd.	Ar^1	RX	Yield (%)
14a	Ph		87
14b	4-Cl-C_6H_4		83
15a	Ph	MeI	92
15b	Ph	EtBr	81
15c	Ph	*n*PrBr	76
15d	Ph	*n*BuBr	84
15e	Ph	$PhCH_2Cl$	88
15f	Ph	$ClCH_2CN$	83
15g	Ph	$ClCH_2COOEt$	91
15h	4-Cl-C_6H_4	MeI	82
15i	4-Cl-C_6H_4	EtBr	74
15j	4-Cl-C_6H_4	*n*PrBr	80
15k	4-Cl-C_6H_4	*n*BuBr	84
15l	4-Cl-C_6H_4	$PhCH_2Cl$	78
15m	4-Cl-C_6H_4	$ClCH_2CN$	77
15n	4-Cl-C_6H_4	$ClCH_2COOEt$	84
17	Ph		43



Scheme 6. Reaction conditions: (i) CO_2, CH_2Cl_2, room temp., 30 h

spectroscopic data for **7a** show the signals of C=O and CH_3 at δ = 154.8 and 20.6 ppm, respectively. The mass spectrum of **7a** shows a strong molecular ion peak at m/z = 367 with 100% abundance.

Conclusion

We have developed an efficient synthesis of 2-substituted 1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-ones by aza-Wittig reactions. This method utilizes easily accessible starting materials and allows mild reaction conditions, straightforward product isolation and good yields. We think that the synthetic approach discussed here compares very favourably with existing methods.

Experimental Section

General Remarks: Melting points are uncorrected. Mass spectra were measured on a Finnigan Trace MS spectrometer. IR were recorded on a PE-983 infrared spectrometer as KBr pellets with absorptions given in cm^{-1}. NMR were recorded in $CDCl_3$ or [D_6]DMSO on a Varian Mercury 400 spectrometer and resonances are given in ppm (δ) relative to TMS. Elementary analyses were determined on a Perkin−Elmer CHN 2400 elementary analysis instrument.

3-Amino-2-arylamino-4(3*H*)-quinazolinones (4): Aromatic isocyanate (5 mmol) was added under nitrogen, at room temperature, to a solution of iminophosphorane **1**[27] (2.12 g, 5 mmol) in dry dichloromethane (15 mL). After leaving the reaction mixture to stand for 6−12 hours at 0−5 °C, the solvent was removed under reduced pressure and diethyl ether/petroleum ether (1:2, 20 mL) was added to precipitate the triphenylphosphane oxide. The mixture was then filtered and the solvent was removed to give carbodiimide **2**, which was used directly without further purification. A solution of hydrazine hydrate (0.35 g, 6 mmol, 85%) in EtOH (5 mL) was added to the solution of **2** prepared above, in EtOH (15 mL). The mixture was stirred for 10 min at room temperature and filtered to give 3-amino-2-arylamino-4(3*H*)-quinazolinone **4**.

3-Amino-2-(phenylamino)-4(3*H*)-quinazolinone (4a): White solid (yield 1.02 g, 81%), m.p. 149−150 °C; ref.[31a] m.p. 150 °C.

3-Amino-2-[(4-chlorophenyl)amino]-4(3*H*)-quinazolinone (4b): White solid (yield 1.03 g, 72%); m.p. 232−233 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.65 (s, 2 H, NH_2), 7.09−8.08 (m, 8 H, Ar-H), 8.71 (s, 1 H, N-H) ppm. IR (KBr): $\tilde{\nu}$ = 3324, 3296, 3219 (N−H), 1677 (C=O), 1613, 1544, 763 cm^{-1}. MS: m/z = 288/286 (35/100) [M^+], 269 (41), 255 (61), 220 (39), 161 (43), 90 (73). $C_{14}H_{11}ClN_4O$ (286.7): calcd. C 58.65, H 3.87, N 19.54; found C 58.82, H 3.75, N 19.58.

***N*-(2-Arylamino-3*H*-quinazolin-4-on-3-yl)iminotriphenylphosphoranes 5a and 5b):** NEt_3 (2.42 g, 24 mmol) was added dropwise, at room temperature, to a mixture of **4** (8 mmol), PPh_3 (3.14 g, 12 mmol) and C_2Cl_6 (2.84 g, 12 mmol) in dry CH_2Cl_2 (40 mL). The colour of the reaction mixture quickly turned yellow. After stirring for 4−6 h, the solvent was removed under reduced pressure and the residue was recrystallized from EtOH to give iminophosphoranes **5**.

***N*-(2-Phenylamino-3*H*−quinazolin-4-on-3-yl)iminotriphenylphosphorane (5a):** White crystals (yield 3.49 g, 85%); m.p. 209−211 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.05−8.03 (m, 24 H, Ar-H), 9.16 (s, 1 H, N-H) ppm. ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 43.70 ppm. IR (KBr): $\tilde{\nu}$ = 3367 (N−H), 1699 (C=O), 1587, 1473, 1115, 690 cm^{-1}. MS: m/z = 512 (81) [M^+], 420 (15), 276 (96), 262 (83), 183 (100), 108 (74). $C_{32}H_{25}N_4OP$ (512.6): calcd. C 74.99, H 4.92, N 10.93; found C 74.84, H 4.81, N 10.96.

***N*-[2-(4-Chlorophenyl)amino-3*H*-quinazolin-4-on-3-yl]iminotriphenylphosphorane (5b):** White crystals (yield 3.33 g, 76%); m.p. 278−280 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.06−8.01 (m, 23 H, Ar-H), 9.42 (s, 1 H, N-H) ppm. ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 43.67 ppm. IR (KBr): $\tilde{\nu}$ = 3372 (N−H), 1698 (C=O), 1583, 1472, 1113, 755 cm^{-1}. MS: m/z = 548/546 (25/77) [M^+], 277 (100), 261 (65), 183 (80), 107 (22). $C_{32}H_{24}ClN_4OP$ (547.0): calcd. C 70.27, H 4.42, N 10.24; found C 70.32, H 4.28, N 10.37.

2-Arylamino-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-ones 7a−7j: Aromatic isocyanate (2 mmol) was added under nitrogen, at room temperature, to a solution of iminophosphorane **5** (2 mmol) in dry dichloromethane (15 mL). The colour of the reaction mixture turned red, disappearing after a few minutes. The colourless solution was stirred at room temperature for 1−2 h. The white precipitate was collected by filtration and recrystallized from CH_2Cl_2/ethanol to give **7** as a crystalline solid.

2-[(4-Methylphenyl)amino]-3-phenyl-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-one (7a): White crystals (yield 664 mg, 90%); m.p. >300 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.33 (s, 3 H, CH_3), 6.12 (s, 1 H, NH), 7.17−7.72 (m, 12 H, Ar-H), 8.44 (d, J = 8.0 Hz, 1 H, H-8) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.6 (CH_3), 114.9, 118.6, 121.1, 125.8, 128.1, 128.2, 128.6, 130.4, 132.1, 132.2, 134.3, 136.6, 137.1, 137.8, 143.4, 149.9 (Ar-C), 154.8 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3295 (N−H), 1675 (C=O), 1579, 1474, 760 cm^{-1}. MS: m/z = 367 (100) [M^+], 351 (22), 248 (14), 221 (34), 119 (38). $C_{22}H_{17}N_5O$ (367.4): calcd. C 71.92, H 4.66, N 19.06; found C 71.81, H 4.69, N 19.25.

2-[(3-Methylphenyl)amino]-3-phenyl-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-one (7b): White crystals (yield 661 mg, 90%); m.p. >300 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.31 (s, 3 H, CH_3), 6.32 (s, 1 H, NH), 7.17−8.00 (m, 12 H, Ar-H), 8.43 (d, J = 8.4 Hz, 1 H, H-8) ppm. IR (KBr): $\tilde{\nu}$ = 3238 (N−H), 1676 (C=O), 1584, 1473, 689 cm^{-1}. MS: m/z = 367 (100) [M^+], 351 (32), 248 (23), 221 (32), 119 (43). $C_{22}H_{17}N_5O$ (367.4): calcd. C 71.92, H 4.66, N 19.06; found C 71.76, H 4.57, N 19.18.

2-(Phenylamino)-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-one (7c): White crystals (yield 652 mg, 92%); m.p. >300 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.18 (s, 1 H, NH), 7.12−7.73 (m, 13 H, Ar-H), 8.45 (d, J = 6.8 Hz, 1 H, H-8) ppm. IR (KBr): $\tilde{\nu}$ = 3277 (N−H), 1673 (C=O), 1579, 1474, 686 cm^{-1}. MS: m/z = 353 (100) [M^+], 337 (22), 235 (37), 221 (54), 77 (85). $C_{21}H_{15}N_5O$ (353.4): calcd. C 71.38, H 4.28, N 19.82; found C 71.45, H 4.22, N 19.71.

2-[(4-Chlorophenyl)amino]-3-phenyl-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-one (7d): White crystals (yield 728 mg, 94%); m.p. >300 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.23 (s, 1 H, NH), 7.10−7.78 (m, 12 H, Ar-H), 8.44 (d, J = 8.0 Hz, 1 H, H-8) ppm. IR (KBr): $\tilde{\nu}$ = 3279 (N−H), 1672 (C=O), 1576, 1474, 763 cm^{-1}. MS: m/z = 389/387 (35/100) [M^+], 371 (11), 236 (9), 221 (22), 77 (32). $C_{21}H_{14}ClN_5O$ (387.8): calcd. C 65.04, H 3.64, N 18.06; found C 65.23, H 3.53, N 18.13.

2-[(3-Chlorophenyl)amino]-3-phenyl-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-one (7e): White crystals (yield 714 mg, 92%); m.p. >300 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.18 (s, 1 H, NH), 7.08−7.74 (m, 12 H, Ar-H), 8.45 (d, J = 8.0 Hz, 1 H, H-8) ppm. IR (KBr): $\tilde{\nu}$ = 3264 (N−H), 1675 (C=O), 1578, 1475, 767 cm^{-1}. MS: m/z = 389/387 (1/3) [M^+], 371 (1), 235 (2), 221 (14), 102 (100).

$C_{21}H_{14}ClN_5O$ (387.8): calcd. C 65.04, H 3.64, N 18.06; found C 65.15, H 3.79, N 17.98.

3-(4-Chlorophenyl)-2-[(4-methylphenyl)amino]-1,2,4-triazolo[5,1-*b*]-quinazolin-9(3*H*)-one (7f): White crystals (yield 745 mg, 93%); m.p. >300 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.32 (s, 3 H, CH_3), 6.18 (s, 1 H, NH), 7.14−7.69 (m, 11 H, Ar-H), 8.42 (d, J = 8.0 Hz, 1 H, H-8) ppm. IR (KBr): $\tilde{\nu}$ = 3287 (N−H), 1673 (C=O), 1577, 1472, 761 cm^{-1}. MS: m/z = 403/401 (37/100) [M$^+$], 385 (9), 256 (14), 221 (12), 102 (44). $C_{22}H_{16}ClN_5O$ (401.9): calcd. C 65.76, H 4.01, N 17.43; found C 65.58, H 4.16, N 17.48.

3-(4-Chlorophenyl)-2-[(3-methylphenyl)amino]-1,2,4-triazolo[5,1-*b*]-quinazolin-9(3*H*)-one (7g): White crystals (yield 740 mg, 92%); m.p. >300 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.35 (s, 3 H, CH_3), 6.10 (s, 1 H, NH), 6.93−7.69 (m, 11 H, Ar-H), 8.44 (d, J = 8.0 Hz, 1 H, H-8) ppm. IR (KBr): $\tilde{\nu}$ = 3276 (N−H), 1673 (C=O), 1589, 1473, 759 cm^{-1}. MS: m/z = 403/401 (10/29) [M$^+$], 385 (6), 256 (12), 221 (10), 102 (100). $C_{22}H_{16}ClN_5O$ (401.9): calcd. C 65.76, H 4.01, N 17.43; found C 65.64, H 3.95, N 17.54.

3-(4-Chlorophenyl)-2-(phenylamino)-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-one (7h): White crystals (yield 704 mg, 91%); m.p. >300 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.16 (s, 1 H, NH), 7.14−7.70 (m, 12 H, Ar-H), 8.44 (d, J = 6.8 Hz, 1 H, H-8) ppm. IR (KBr): $\tilde{\nu}$ = 3263 (N−H), 1673 (C=O), 1576, 1473, 757 cm^{-1}. MS: m/z = 389/387 (11/31) [M$^+$], 371 (5), 242 (7), 207 (7), 102 (100). $C_{21}H_{14}ClN_5O$ (387.8): calcd. C 65.04, H 3.64, N 18.06; found C 65.23, H 3.56, N 18.16.

3-(4-Chlorophenyl)-2-[(4-chlorophenyl)amino]-1,2,4-triazolo[5,1-*b*]-quinazolin-9(3*H*)-one (7i): White crystals (yield 733 mg, 87%); m.p. >300 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.18 (s, 1 H, NH), 7.18−7.72 (m, 11 H, Ar-H), 8.44 (d, J = 8.0 Hz, 1 H, H-8) ppm. IR (KBr): $\tilde{\nu}$ = 3271 (N−H), 1670 (C=O), 1575, 1471, 764 cm^{-1}. MS: m/z = 423/421 (4/6) [M$^+$], 255 (5), 241 (4), 144 (17), 102 (100). $C_{21}H_{13}Cl_2N_5O$ (422.3): calcd. C 59.73, H 3.10, N 16.58; found C 59.78, H 3.23, N 16.41.

3-(4-Chlorophenyl)-2-[(3-chlorophenyl)amino]-1,2,4-triazolo[5,1-*b*]-quinazolin-9(3*H*)-one (7j): White crystals (yield 726 mg, 86%); m.p. >300 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.16 (s, 1 H, NH), 7.16−7.70 (m, 11 H, Ar-H), 8.44 (d, J = 8.0 Hz, 1 H, H-8) ppm. IR (KBr): $\tilde{\nu}$ = 3281 (N−H), 1656 (C=O), 1586, 1477, 767 cm^{-1}. MS: m/z = 423/421 (1.3/2) [M$^+$], 255 (5), 241 (4), 145 (21), 102 (100). $C_{21}H_{13}Cl_2N_5O$ (422.3): calcd. C 59.73, H 3.10, N 16.58; found C 59.94, H 3.21, N 16.43.

1,2,4-Triazolo[5,1-*b*]quinazolin-9(3*H*)-ones 9a−9i: Acyl chloride (2 mmol) and triethylamine (0.20 g, 2 mmol) were added under nitrogen, at room temperature, to a solution of iminophosphorane **5** (2 mmol) in dry CH_2Cl_2 (15 mL). The solution was stirred at room temperature for 2−4 h. The white precipitated ammonium salt was separated by filtration and the filtrate was concentrated to dryness. The residue was recrystallized from CH_2Cl_2/ethanol to give **9** as a crystalline solid.

2-Methyl-3-phenyl-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-one (9a): White crystals (yield 404 mg, 73%); m.p. 290−291 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.47 (s, 3 H, CH_3), 7.26−7.71 (m, 8 H, Ar-H), 8.46 (d, J = 8.0 Hz, 1 H, H-8) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.6 (CH_3), 114.6, 118.9, 127.3, 127.8, 128.1, 129.0, 131.7, 133.7, 137.2, 138.4, 145.3, 153.4 (Ar-C), 154.3 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 1698 (C=O), 1608, 1593, 1471, 764 cm^{-1}. MS: m/z = 276 (100) [M$^+$], 247 (13), 236 (14), 219 (12), 118 (27), 77 (85). $C_{16}H_{12}N_4O$ (276.3): calcd. C 69.55, H 4.38, N 20.28; found C 69.72, H 4.30, N 20.33.

2,3-Diphenyl-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-one (9b): White crystals (yield 595 mg, 88%); m.p. >300 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.19−7.65 (m, 13 H, Ar-H), 8.42 (d, J = 8.0 Hz, 1 H, H-8) ppm. IR (KBr): $\tilde{\nu}$ = 1699 (C=O), 1628, 1552, 1470, 770 cm^{-1}. MS: m/z = 338 (5) [M$^+$], 219 (4), 180 (35), 102 (100). $C_{21}H_{14}N_4O$ (338.4): calcd. C 74.54, H 4.17, N 16.56; found C 74.58, H 4.26, N 16.41.

2-(4-Chlorophenyl)-3-phenyl-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-one (9c): White crystals (yield 500 mg, 67%); m.p. 194−195 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.35−7.76 (m, 12 H, Ar-H), 8.49 (d, J = 8.0 Hz, 1 H, H-8) ppm. IR (KBr): $\tilde{\nu}$ = 1701 (C=O), 1608, 1591, 1470, 743 cm^{-1}. MS: m/z = 374/372 (28/81) [M$^+$], 371 (100), 308 (5), 235 (6), 102 (42), 77 (83). $C_{21}H_{13}ClN_4O$ (372.8): calcd. C 67.66, H 3.51, N 15.03; found C 67.82, H 3.35, N 15.14.

2-Chloromethyl-3-phenyl-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-one (9d): White crystals (yield 390 mg, 63%); m.p. 221−223 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.62 (s, 2 H, $ClCH_2$), 7.38−7.71 (m, 8 H, Ar-H), 8.40 (d, J = 8.0 Hz, 1 H, H-8) ppm. IR (KBr): $\tilde{\nu}$ = 1705 (C=O), 1628, 1610, 1473, 764 cm^{-1}. MS: m/z = 312/310 (35/100) [M$^+$], 275 (70), 236 (34), 208 (21), 102 (93). $C_{16}H_{11}ClN_4O$ (310.8): calcd. C 61.84, H 3.57, N 18.03; found C 61.76, H 3.63, N 18.26.

2-[(4-Chlorophenoxy)methyl]-3-phenyl-1,2,4-triazolo[5,1-*b*]-quinazolin-9(3*H*)-one (9e): White crystals (yield 626 mg, 78%); m.p. 175−176 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.18 (s, 2 H, OCH_2), 6.80−7.82 (m, 12 H, Ar-H), 8.44 (d, J = 7.6 Hz, 1 H, H-8) ppm. IR (KBr): $\tilde{\nu}$ = 1705 (C=O), 1627, 1609, 1473, 769 cm^{-1}. MS: m/z = 404/402 (30/85) [M$^+$], 275 (100), 235 (22), 218 (26), 102 (85). $C_{22}H_{15}ClN_4O_2$ (402.8): calcd. C 65.60, H 3.75, N 13.91; found C 65.45, H 3.84, N 13.83.

3-(4-Chlorophenyl)-2-methyl-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-one (9f): White crystals (yield 424 mg, 68%); m.p. >300 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.48 (s, 3 H, CH_3), 7.37−7.72 (m, 7 H, Ar-H), 8.46 (d, J = 8.0 Hz, 1 H, H-8) ppm. IR (KBr): $\tilde{\nu}$ = 1688 (C=O), 1628, 1609, 1473, 770 cm^{-1}. MS: m/z = 312/310 (33/93) [M$^+$], 309 (100), 275 (18), 235 (64), 152 (46), 111 (92). $C_{16}H_{11}ClN_4O$ (310.8): calcd. C 61.84, H 3.57, N 18.03; found C 61.90, H 3.36, N 18.17.

3-(4-Chlorophenyl)-2-phenyl-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-one (9g): White crystals (yield 604 mg, 81%); m.p. 284−286 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.38−7.74 (m, 12 H, Ar-H), 8.49 (d, J = 8.0 Hz, 1 H, H-8) ppm. IR (KBr): $\tilde{\nu}$ = 1704 (C=O), 1629, 1608, 1403, 754 cm^{-1}. MS: m/z = 374/372 (31/90) [M$^+$], 371 (100), 336 (34), 279 (16), 214 (22), 102 (97). $C_{21}H_{13}ClN_4O$ (372.8): calcd. C 67.66, H 3.51, N 15.03; found C 67.57, H 3.46, N 15.27.

2,3-Bis(4-Chlorophenyl)-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-one (9h): White crystals (yield 592 mg, 73%); m.p. >300 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.38−7.76 (m, 11 H, Ar-H), 8.47 (d, J = 8.0 Hz, 1 H, H-8) ppm. IR (KBr): $\tilde{\nu}$ = 1684 (C=O), 1606, 1586, 1474, 763 cm^{-1}. MS: m/z = 410/408/406 (8/46/72) [M$^+$], 370 (11), 248 (12), 137 (31), 102 (100). $C_{21}H_{12}Cl_2N_4O$ (407.3): calcd. C 61.93, H 2.97, N 13.76; found C 61.81, H 2.95, N 13.88.

2-Chloromethyl-3-(4-chlorophenyl)-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-one (9i): White crystals (yield 465 mg, 67%); m.p. 205−207 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.62 (s, 2 H, $ClCH_2$), 7.40−7.73 (m, 7 H, Ar-H), 8.43 (d, J = 8.4 Hz, 1 H, H-8) ppm. IR (KBr): $\tilde{\nu}$ = 1695 (C=O), 1635, 1611, 1472, 766 cm^{-1}. MS: m/z = 348/346/344 (4/22/34) [M$^+$], 313 (96), 270 (54), 255 (86), 90 (100). $C_{16}H_{10}Cl_2N_4O$ (345.2): calcd. C 55.67, H 2.92, N 16.23; found C 55.41, H 2.76, N 16.38.

2-Thioxo-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-ones 14a, and 14b: An excess of CS_2 (10 mL) was added under nitrogen, at room temperature, to a solution of iminophosphorane **5** (30 mmol) in dry dichloromethane (15 mL). After refluxing the reaction mixture for 20 h, the white precipitated solid was collected by filtration to give **14**.

3-Phenyl-2-thioxo-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-one (14a): White crystals (yield 7.67 g, 87%); m.p. 278−280 °C. ^{1}H NMR ([D$_6$]DMSO, 400 MHz): δ = 7.40−7.79 (m, 8 H, Ar-H), 8.26 (d, J = 8.4 Hz, 1 H, 8-H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 114.7, 118.8, 127.4, 128.1, 128.8, 131.6, 134.0, 136.8, 138.2, 145.2 153.6 (Ar-C), 154.1 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3423 (N−H), 1702 (C=O), 1657, 1578, 1126, 685 cm^{-1}. MS: m/z = 294 (2) [M$^+$], 265 (2), 235 (4), 144 (26), 77 (100). $C_{15}H_{10}N_4OS$ (294.3): calcd. C 61.21, H 3.42, N 19.03; found C 61.14, H 3.35, N 19.24.

3-(4-Chlorophenyl)-2-thioxo-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-one (14b): White crystals (yield 8.18 g, 83%); m.p. 267−268 °C. ^{1}H NMR ([D$_6$]DMSO, 400 MHz): δ = 7.39−7.79 (m, 7 H, Ar-H), 8.25 (d, J = 8.0 Hz, 1 H, 8-H) ppm. IR (KBr): $\tilde{\nu}$ = 3424 (N−H), 1718 (C=O), 1663, 1579, 1134, 756 cm^{-1}. MS: m/z = 330/328 (32/100) [M$^+$], 265 (17), 235 (12), 101 (12), 77 (11). $C_{15}H_9ClN_4OS$ (328.7): calcd. C 54.80, H 2.76, N 17.04; found C 54.96, H 2.62, N 17.08.

2-Alkylthio-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-ones 15a−15n: A mixture of **14** (4 mmol), alkyl halide (5 mmol) and solid potassium carbonate (1.11 g, 8 mmol) in CH_3CN (30 mL) was stirred for 1−4 h at room temperature or 50−60 °C and then filtered. The filtrate was condensed and the residue was recrystallized from dichloromethane/petroleum ether (1:2) to give 2-alkylthio-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-ones **15**.

2-(Methylthio)-3-phenyl-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-one (15a): White crystals (yield 1.13 g, 92%); m.p. 296−298 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.81 (s, 3 H, CH_3), 7.40−7.71 (m, 8 H, Ar-H), 8.45 (d, J = 8.0 Hz, 1 H, H-8) ppm. IR (KBr): $\tilde{\nu}$ = 1696 (C=O), 1607, 1510, 1469, 762 cm^{-1}. MS: m/z = 308 (77) [M$^+$], 293 (100), 265 (9), 221 (7), 102 (40), 77 (42). $C_{16}H_{12}N_4OS$ (308.4): calcd. C 62.32, H 3.92, N 18.17; found C 62.17, H 3.84, N 18.30.

2-(Ethylthio)-3-phenyl-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-one (15b): White crystals (yield 1.05 g, 81%); m.p. 233−235 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.48 (t, J = 7.2 Hz, 3 H, CH_3), 3.43 (q, J = 7.2 Hz, 2 H, SCH_2), 7.37−7.69 (m, 8 H, Ar-H), 8.45 (d, J = 8.4 Hz, 1 H, H-8) ppm. IR (KBr): $\tilde{\nu}$ = 1693 (C=O), 1633, 1506, 1470, 767 cm^{-1}. MS: m/z = 322 (94) [M$^+$], 293 (100), 265 (8), 236 (17), 221 (35), 102 (76), 77 (79). $C_{17}H_{14}N_4OS$ (322.4): calcd. C 63.34, H 4.38, N 17.38; found C 63.42, H 4.21, N 17.32.

3-Phenyl-2-(*n*-propylthio)-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-one (15c): White crystals (yield 1.02 g, 76%); m.p. 218−220 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.07 (t, J = 7.2 Hz, 3 H, CH_3), 1.80−1.89 (m, 2 H, CH_2), 3.41 (t, J = 7.2 Hz, 2 H, SCH_2), 7.37−7.69 (m, 8 H, Ar-H), 8.45 (d, J = 8.0 Hz, 1 H, H-8) ppm. IR (KBr): $\tilde{\nu}$ = 1695 (C=O), 1632, 1508, 1469, 768 cm^{-1}. MS: m/z = 336 (59) [M$^+$], 293 (58), 236 (11), 221 (15), 102 (62), 41 (100). $C_{18}H_{16}N_4OS$ (336.4): calcd. C 64.27, H 4.79, N 16.65; found C 64.21, H 4.85, N 16.52.

2-(*n*-Butylthio)-3-phenyl-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-one (15d): White crystals (yield 1.18 g, 84%); m.p. 191−192 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.95 (t, J = 7.2 Hz, 3 H, CH_3), 1.44−1.81 (m, 4 H, CH_2CH_2), 3.43 (t, J = 7.2 Hz, 2 H, SCH_2), 7.37−7.69 (m, 8 H, Ar-H), 8.45 (d, J = 8.0 Hz, 1 H, H-8) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 13.4 (CH_3), 21.7 (CH_2), 30.4 (CH_2), 31.2 (SCH_2), 117.7, 123.5, 126.0, 127.2, 129.8, 130.1, 131.3, 133.8, 147.1, 148.4, 154.3 (Ar-C), 155.5 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 1704 (C=O), 1627, 1509, 1466, 763 cm^{-1}. MS: m/z = 350 (3) [M$^+$], 293 (18), 236 (4), 221 (4), 102 (57), 41 (100). $C_{19}H_{18}N_4OS$ (350.5): calcd. C 65.12, H 5.18, N 15.99; found C 65.06, H 5.03, N 16.17.

3-Phenyl-2-(phenylmethylthio)-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-one (15e): White crystals (yield 1.35 g, 88%); m.p. 216−218 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.65 (s, 2 H, SCH_2), 7.32−7.72 (m, 13 H, Ar-H), 8.46 (d, J = 8.0 Hz, 1 H, H-8) ppm. IR (KBr): $\tilde{\nu}$ = 1702 (C=O), 1631, 1510, 1468, 764 cm^{-1}. MS: m/z = 384 (57) [M$^+$], 324 (7), 293 (23), 236 (12), 148 (58), 91 (100). $C_{22}H_{16}N_4OS$ (384.5): calcd. C 68.73, H 4.19, N 14.57; found C 68.54, H 4.32, N 14.74.

2-(Cyanomethylthio)-3-phenyl-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-one (15f): White crystals (yield 1.11 g, 83%); m.p. 251−253 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.25 (s, 2 H, SCH_2), 7.42−7.73 (m, 8 H, Ar-H), 8.45 (d, J = 7.6 Hz, 1 H, H-8) ppm. IR (KBr): $\tilde{\nu}$ = 2246 (CN), 1698 (C=O), 1631, 1511, 1468, 770 cm^{-1}. MS: m/z = 333 (87) [M$^+$], 293 (84), 235 (24), 130 (97), 102 (100). $C_{17}H_{11}N_5OS$ (333.4): calcd. C 61.25, H 3.33, N 21.01; found C 61.10, H 3.22, N 21.07.

2-(Ethoxycarbonylmethylthio)-3-phenyl-1,2,4-triazolo[5,1-*b*]-quinazolin-9(3*H*)-one (15g): White crystals (yield 1.38 g, 91%); m.p. 230−231 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.33 (t, J = 7.2 Hz, 3 H, CH_3), 4.24−4.29 (m, 4 H, SCH_2 and OCH_2), 7.37−7.73 (m, 8 H, Ar-H), 8.44 (d, J = 7.6 Hz, 1 H, H-8) ppm. IR (KBr): $\tilde{\nu}$ = 1723 and 1699 (C=O), 1632, 1512, 1467, 765 cm^{-1}. MS: m/z = 380 (96) [M$^+$], 335 (11), 307 (12), 293 (100), 221 (14), 102 (83). $C_{19}H_{16}N_4O_3S$ (380.4): calcd. C 59.99, H 4.24, N 14.73; found C 60.03, H 4.10, N 14.67.

3-(4-Chlorophenyl)-2-(methylthio)-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-one (15h): White crystals (yield 1.12 g, 82%); m.p. 274−275 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.80 (s, 3 H, CH_3), 7.36−7.73 (m, 7 H, Ar-H), 8.44 (d, J = 8.4 Hz, 1 H, H-8) ppm. IR (KBr): $\tilde{\nu}$ = 1679 (C=O), 1630, 1510, 1462, 771 cm^{-1}. MS: m/z = 344/342 (35/100) [M$^+$], 327 (97), 292 (29), 255 (43), 130 (94). $C_{16}H_{11}ClN_4OS$ (342.8): calcd. C 56.06, H 3.23, N 16.34; found C 56.13, H 3.21, N 16.57.

3-(4-Chlorophenyl)-2-(ethylthio)-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-one (15i): White crystals (yield 1.06 g, 74%); m.p. >300 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.50 (t, J = 7.2 Hz, 3 H, CH_3), 3.45 (q, J = 7.2 Hz, 2 H, SCH_2), 7.38−7.70 (m, 7 H, Ar-H), 8.45 (d, J = 7.2 Hz, 1 H, H-8) ppm. IR (KBr): $\tilde{\nu}$ = 1690 (C=O), 1646, 1501, 1473, 769 cm^{-1}. MS: m/z = 358/356 (31/98) [M$^+$], 327 (100), 292 (17), 255 (31), 102 (75). $C_{17}H_{13}ClN_4OS$ (356.8): calcd. C 57.22, H 3.67, N 15.70; found C 57.36, H 3.41, N 15.59.

3-(4-Chlorophenyl)-2-(*n*-propylthio)-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-one (15j): White crystals (yield 1.18 g, 80%); m.p. 188−189 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.08 (t, J = 7.2 Hz, 3 H, CH_3), 1.81−1.89 (m, 2 H, CH_2), 3.42 (t, J = 7.2 Hz, 2 H, SCH_2), 7.38−7.71 (m, 7 H, Ar-H), 8.44 (d, J = 8.0 Hz, 1 H, H-8) ppm. IR (KBr): $\tilde{\nu}$ = 1689 (C=O), 1636, 1511, 1473, 770 cm^{-1}. MS: m/z = 372/370 (30/83) [M$^+$], 327 (100), 292 (20), 235 (27), 102 (66). $C_{18}H_{15}ClN_4OS$ (370.9): calcd. C 58.30, H 4.08, N 15.11; found C 58.15, H 4.13, N 15.17.

2-(*n*-Butylthio)-3-(4-chlorophenyl)-1,2,4-triazolo[5,1-*b*]quinazolin-9(3*H*)-one (15k): White crystals (yield 1.29 g, 84%); m.p. 166−168 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.96 (t, J = 7.2 Hz, 3 H, CH_3), 1.43−1.81 (m, 4 H, CH_2CH_2), 3.45 (t, J = 7.2 Hz, 2 H, SCH_2), 7.38−7.70 (m, 7 H, Ar-H), 8.45 (d, J = 8.0 Hz, 1 H, H-8) ppm. IR (KBr): $\tilde{\nu}$ = 1694 (C=O), 1633, 1608, 1510, 1472, 768 cm^{-1}. MS: m/z = 386/384 (27/75) [M$^+$], 237 (36), 327 (100), 255 (28), 235 (31), 102 (72). $C_{19}H_{17}ClN_4OS$ (384.9): calcd. C 59.29, H 4.45, N 14.56; found C 59.14, H 4.67, N 14.48.

3-(4-Chlorophenyl)-2-(phenylmethylthio)-1,2,4-triazolo[5,1-*b*]-quinazolin-9(3*H*)-one (15l): White crystals (yield 1.30 g, 78%); m.p. 191−193 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.65 (s, 2 H, SCH_2), 7.31−7.72 (m, 12 H, Ar-H), 8.46 (d, J = 8.0 Hz, 1 H, H-8) ppm. IR (KBr): $\tilde{\nu}$ = 1689 (C=O), 1628, 1508, 1471, 766 cm^{-1}. MS: m/z = 420/418 (4/12) [M$^+$], 372 (12), 296 (67), 270 (96), 235

(68), 145 (97), 91 (100). $C_{22}H_{15}ClN_4OS$ (418.9): calcd. C 63.08, H 3.61, N 13.37; found C 63.25, H 3.45, N 13.24.

3-(4-Chlorophenyl)-2-(cyanomethylthio)-1,2,4-triazolo[5,1-*b*]-quinazolin-9(3*H*)-one (15m): White crystals (yield 1.13 g, 77%); m.p. 238−240 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.25 (s, 2 H, SCH_2), 7.40−7.75 (m, 7 H, Ar-H), 8.44 (d, J = 8.0 Hz, 1 H, H-8) ppm. IR (KBr): $\tilde{\nu}$ = 2238 (CN), 1685 (C=O), 1637, 1518, 1471, 767 cm^{-1}. MS: m/z = 369/367 (20/53) [M^+], 327 (50), 292 (41), 130 (61), 102 (100). $C_{17}H_{10}ClN_5OS$ (367.8): calcd. C 55.51, H 2.74, N 19.04; found C 55.43, H 2.79, N 19.16.

3-(4-Chlorophenyl)-2-(ethoxycarbonylmethylthio)-1,2,4-triazolo[5,1-*b*]-quinazolin-9(3*H*)-one (15n): White crystals (yield 1.40 g, 84%); m.p. 191−193 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.33 (t, J = 7.2 Hz, 3 H, CH_3), 4.24−4.29 (m, 4 H, SCH_2 and OCH_2), 7.37−7.71 (m, 7 H, Ar-H), 8.43 (d, J = 8.0 Hz, 1 H, H-8) ppm. IR (KBr): $\tilde{\nu}$ = 1739 and 1689 (C=O), 1635, 1508, 1470, 767 cm^{-1}. MS: m/z = 416/414 (33/98) [M^+], 369 (16), 327 (98), 292 (29), 130 (62), 102 (100). $C_{19}H_{15}ClN_4O_3S$ (414.9): calcd. C 55.01, H 3.64, N 13.50; found C 55.07, H 3.53, N 13.42.

1,3-Dihydro-3-phenyl-1,2,4-triazolo[5,1-*b*]quinazolin-2,9-dione (17): Dry CO_2 was bubbled through a solution of iminophosphorane **5a** (1.54 g, 3 mmol) in dry dichloromethane (30 mL) at room temperature. After allowing the reaction mixture to stand for 24 h, the white precipitate was collected by filtration to give **17**. White crystals (yield 357 mg, 43%); m.p. >300 °C. ^{1}H NMR ([D$_6$]DMSO, 400 MHz): δ = 7.39−7.75 (m, 8 H, Ar-H), 8.15 (d, J = 8.0 Hz, 1 H, 8-H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 115.4, 120.6, 126.9, 127.6, 128.1, 128.6, 131.0, 132.9, 138.2, 138.8, 142.9 150.1 (Ar-C), 152.6 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3448 (N−H), 1735 and 1698 (C=O), 1637, 1442, 1139, 762 cm^{-1}. MS: m/z = 278 (100) [M^+], 236 (11), 221 (21), 194 (12), 102 (18). $C_{15}H_{10}N_4O_2$ (278.3): calcd. C 64.74, H 3.62, N 20.13; found C 64.57, H 3.54, N 20.18.

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