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Preparation of Fused Tetracyclic Quinazolinones by Combinations of Aza-Wittig Methodologies and Cu^{I}-Catalysed Heteroarylation Processes

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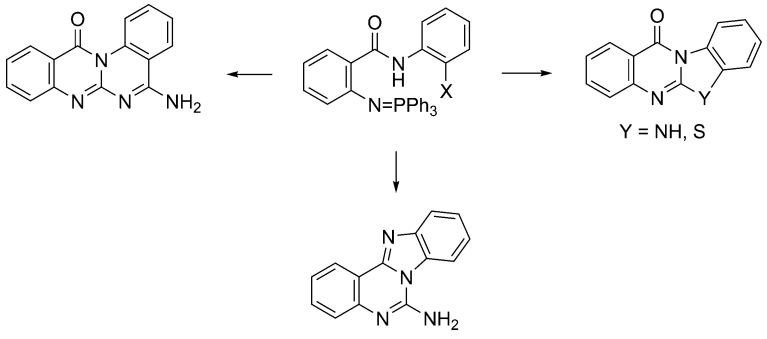
A number of linear quinazolinones fused to five-membered rings – benzimidazo[2,1-*b*]quinazolinones **8** and benzothiazolo[2,3-*b*]quinazolinones **10** – have been prepared from iminophosphoranes **4**, derived from *N*-substituted *o*-azidobenzamides by a combination of the aza-Wittig methodology and Cu^{I}-catalysed heteroarylation. The presence of a nitrogen functionality in the *N*-aryl substituent of **4** promotes heterocyclization after an aza-Wittig reaction/reductive process, either across the 2-position, to afford quinazolino[2,1-*b*]quinazolinones **11**–**14**, or across the 4-position, to afford the benzimidazo[1,2-*c*]quinazoline **16** from the initially formed 3*H*-quinazolin-4-one. When an acetyl group is present in the *N*-aryl substituent of **4**, aza-Wittig reactions with isocyanates lead directly to 4-methylene-4*H*-3,1-benzoxazines **18**; this transformation involves the initial formation of a carbodiimide, which undergoes ring-closure through the enol form of the carboxamide group and eventually an unprecedented iminobenzoxazine/methylenebenzoxazine rearrangement.

Introduction

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

Over the past twenty years, the aza-Wittig reactions of iminophosphoranes have been receiving increasing attention in view of their utility in the synthesis of nitrogen heterocyclic compounds.[5] Among the aza-Wittig methodologies that have been developed, the tandem aza-Wittig/heterocumulene-mediated annulation process allows the preparation of 2-substituted quinazolinone derivatives.[6] This type of heterocyclization reaction is achieved by the use of a functional iminophosphorane bearing an amido group placed at an appropriate position. In particular, iminophosphoranes derived from *N*-aryl-substituted *o*-azidobenzamides react with alkyl or aryl isocyanates to give 2-[alkyl(aryl)amino]quinazolin-4(3*H*)-ones.[7]



Scheme 1. Fused quinazoline derivatives from *o*-functionalized (arylimino)phosphoranes.

We now wish to report an extension of this methodology that paves the way for the preparation of the not readily available linear or angular tetracyclic ring systems incorporating quinazoline moieties. Our approach is based on the

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use of (arylimino)phosphoranes bearing *N*-(*o*-substituted-aryl)amide substituents at their *ortho*-positions (Scheme 1). These building blocks first undergo an aza-Wittig/heterocumulene-mediated cyclization process on treatment with isocyanates and carbon disulfide to give the expected 2-amino- or 2-mercapto-substituted quinazolinones. These intermediate products are able to undergo a plethora of heterocyclization reactions depending on the nature of the functional groups present at the *N*-aryl substituents, as well as on the functionality generated at the quinazolinone ring 2-positions. Several combinations could give rise to the target tetracyclic ring systems through second cyclization processes across either the 2-positions or the 4-positions of the preformed quinazoline rings (Scheme 1).

Results and Discussion

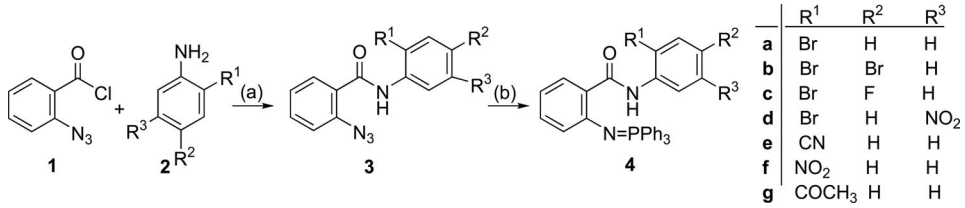
The starting iminophosphoranes **4** (Scheme 2) have been prepared by the following two-step process: (a) acylation of the appropriate arylamines **2** with *o*-azidobenzoyl chloride (**1**)[8] in dichloromethane in the presence of pyridine to give the *N*-aryl-substituted *o*-azidobenzamides **3** in 77–90% yields, and (b) Staudinger reactions between the azides **3** and triphenylphosphane in dichloromethane at room temperature to give the iminophosphoranes **4** in almost quantitative yields (95–98%, Table 1).

Table 1. Compounds **3** and **4** prepared.

Aryl azide **3**	Yield [%]	Iminophosphorane **4**	Yield [%]
3a	90	**4a**	98
3b	75	**4b**	97
3c	86	**4c**	96
3d	85	**4d**	96
3e	78	**4e**	95
3f	85	**4f**	97
3g	77	**4g**	96

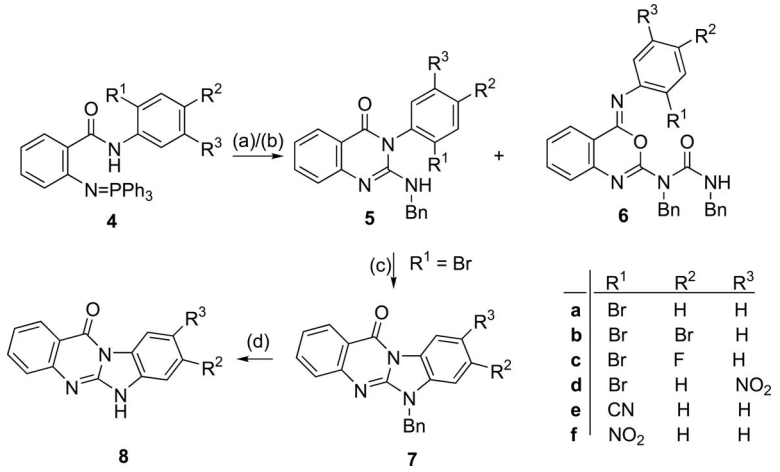
Aza-Wittig reactions between the iminophosphoranes **4a**–**d** and benzyl isocyanate in dry toluene at reflux temperature then provided the 2-benzylamino-substituted quinazolinones **5** in low yields ranging from 5 to 80% (Scheme 3, Table 2). Better yields were obtained when the heating was carried out in *o*-xylene at reflux temperature or under microwave irradiation conditions. Under these conditions, compounds **5** were obtained in high yields from 75 to 87%.

It is important to note that variable amounts of the corresponding 4*H*-3,1-benzoxazine-4-imines **6** were isolated, depending on the reaction conditions, from the aza-Wittig reactions between iminophosphoranes **4** and benzyl isocyanate (Table 2). High yields of quinazolinones **5** are obtained either by heating in *o*-xylene for 5 h or by microwave heating for 15 min, whereas when the reaction is carried out



	R^1	R^2	R^3
a	Br	H	H
b	Br	Br	H
c	Br	F	H
d	Br	H	NO_2
e	CN	H	H
f	NO_2	H	H
g	$COCH_3$	H	H

Scheme 2. Preparation of *o*-functionalized aryl azides **3** and (arylimino)phosphoranes **4**. Reagents and conditions: (a) CH_2Cl_2, anhydrous pyridine, 0 °C → room temp. (77–90%); (b) Ph_3P, CH_2Cl_2, 0 °C → room temp. (95–98%).



	R^1	R^2	R^3
a	Br	H	H
b	Br	Br	H
c	Br	F	H
d	Br	H	NO_2
e	CN	H	H
f	NO_2	H	H

Scheme 3. Preparation of benzimidazo[2,1-*b*]quinazoline-12(5*H*)-ones **8**. Reagents and conditions: (a) BnNCO, toluene, reflux, **5** (5–80%), **6** (10–90%), or microwaves, *o*-xylene, sealed tube, 15 min, **5** (75–87%), **6** (8–20%); (b) BnNCO, *o*-xylene, reflux or microwaves, *o*-xylene, sealed tube; (c) CuI, NaH, diglyme, 100 °C, **7** (70–80%); (d) CF_3COOH, 100 °C, **8** (65–70%).

Table 2. Compounds **5** and **6** prepared.

Compound **5**	Yield [%] [a] ([b])	Compound **6**	Yield [%] [a] ([b])
5a	10 (80)	**6a**	79 (15)
5b	21 (85)	**6b**	70 (10)
5c	5 (85)	**6c**	90 (10)
5d	58 (75)	**6d**	15 (20)
5e	80 (87)	**6e**	10 (8)
5f	20 (85)	**6f**	57 (10)

[a] Yields obtained by heating in toluene. [b] Yields obtained under microwave irradiation conditions.

in toluene at reflux temperature compounds **6** are found to be the major products. We believe that the formation of compounds **6** involves initial aza-Wittig reactions between the iminophosphoranes **4** and benzyl isocyanate to give carbodiimides as highly reactive intermediates that easily undergo ring-closure by nucleophilic attack of the hard end of the carboxamide group (the oxygen atom) on the hard electrophilic sp-hybridized carbon atom of the carbodiimide moiety to give the 3,1-benzoxazine ring with concomitant addition of the second molecule of isocyanate on the formed amino group. When compounds **6** are heated either in *o*-xylene at reflux temperature or in a microwave oven, the quinazolinones **5** are obtained in almost quantitative yields. An unambiguous structural characterization of compound **6d** was achieved by X-ray crystallographic analysis (Figure 1).

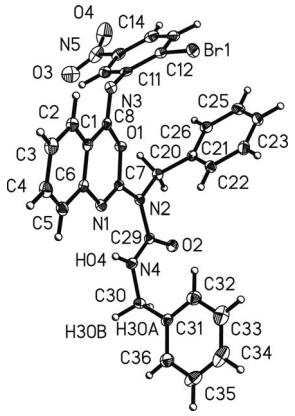


Figure 1. ORTEP view of the molecular structure of **6d** showing the atom labelling.

The 4*H*-benzo[*d*][1,3]oxazin-2-yl derivative **6d** is almost planar (the mean deviation from planarity is 0.047Å and is rotated by just 21.4° with respect to the mean plane of the urea atoms). The two benzyl substituents are rotated by 88.7° and 90.7° with respect to the mean plane of the urea atoms, so the 4*H*-benzo[*d*][1,3]oxazin-2-yl moiety is almost perpendicular to the benzyl substituents on the urea (72.8° and 110.7°). The 4*H*-benzo[*d*][1,3]oxazin-2-yl and the (2-bromo-5-nitrophenyl)imine components are also nearly perpendicular (109.6°). A C30–H30A···N1 intermolecular hydrogen bond is observed in the compound, linking the molecules in a chain parallel to the *b* axis (Table 3).

Table 3. Hydrogen bonds [Å and °] in **6d**.[a]

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)
N(4)–H(04)···N(1)	0.79(2)	2.02(2)	2.646(2)	136(2)
N(4)–H(04)···O(2)#1	0.79(2)	2.59(2)	3.138(2)	127(2)
C(30)H(30A)···N(1)#2	0.99	2.58	3.418(2)	141.9

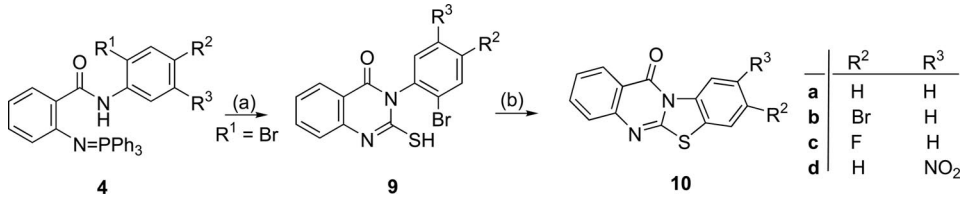
[a] Symmetry transformations used to generate equivalent atoms: #1: $-x + 1$, $y + 1/2$, $-z + 1/2$; #2: $-x + 1$, $y - 1/2$, $-z + 1/2$.

Copper-catalysed C–N bond formation through coupling between amines or amides and aryl halides has received significant attention and has provided a versatile method for the synthesis of a wide range of arylamines.[9] A number of useful synthetic protocols utilizing various combinations of a copper source, a ligand, a base, and a solvent have been developed to achieve high efficiency in Ullmann-type amination reactions of various substrates under mild conditions.[10] Intramolecular Ullmann coupling reactions, on the other hand, have remained less explored. To the best of our knowledge, only a few examples of intramolecular copper-catalysed amination of aryl (or vinyl) halides leading to the formation of indole rings have been reported.[11] With this in mind, quinazolinones **5** may be considered suitable candidates for the generation of fused imidazole rings. In this context, the intramolecular arylamination process was studied. The copper-mediated imidazolization of precursors **5** was carried out with copper(I) iodide in the presence of NaH in bis(2-methoxyethyl) ether at 100 °C to give the corresponding benzimidazo[2,1-*b*]quinazolin-12(5*H*)-ones **7** in 70–80% yields (Scheme 3, Table 4). Removal of the benzyl groups by treatment with neat trifluoroacetic acid[12] provided compounds **8** in 65–70% yields (Table 4). This tetracyclic ring system has been prepared previously,[13] and has been found to present promising antitumour activity, with the benzimidazole and quinazoline moieties serving to intercalate DNA, thereby effectively truncating proliferation of human tumour cell lines.[14]

Table 4. Compounds **7** and **8** prepared.

Compound	Yield [%]	Compound	Yield [%]
7a	80	**8a**	70
7b	75	**8b**	68
7c	70	**8c**	65
7d	73	**8d**	66

Iminophosphoranes **4a**–**d** also reacted in aza-Wittig-type fashion with carbon disulfide to provide functionalized aryl isothiocyanates (Scheme 4), which under thermal conditions underwent cyclization to give the 2-thio-substituted quinazolinones **9** in 70–80% yields. Similar CuI-catalysed *S*-arylation yielded the benzothiazolo[2,3-*b*]quinazolinones **10** in 72–80% yields (Table 5). A number of synthetic methods for the preparation of this ring system have been developed. These include reactions between heteroaromatic 2-amino esters and 2-(methylthio)-2-thiazoline,[15] solid-phase methods,[16] condensations of substituted anthranilic acids or esters with methyl 2-chlorothiazole-5-carboxylate,[17] and the electrochemical oxidation of catechols in the presence of 2-mercapto-3*H*-quinazolin-4-one.[18]



Scheme 4. Preparation of benzothiazolo[2,3-*b*]quinazoline-12(5*H*)-ones **10**. Reagents and conditions: (a) CS_2, sealed tube, toluene, 100 °C (60–74%); (b) CuI, NaH, diglyme, 150 °C (72–80%).

Table 5. Compounds **9** and **10** prepared.

Compound	Yield [%]	Compound	Yield [%]
9a	70	**10a**	75
9b	74	**10b**	72
9c	63	**10c**	80
9d	60		

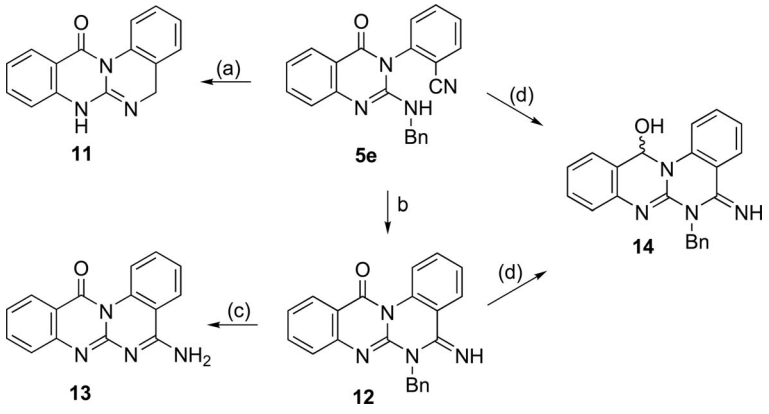
The capability of functionalized quinazolinones **5** to afford the quinazolino-quinazoline ring system is clearly illustrated by the behaviour of quinazolinone **5e** towards different reducing agents. At first, the hydrogenation of the cyano functionality was accomplished with Pd/C in the presence of formic acid. The dihydroquinazolinone-annulated product **11** (Scheme 5) was isolated in 80% yield. In view of the number of steps involved in the formation of **11** – (a) reduction of the nitrile group to a primary amine, (b) removal of the benzyl group and concomitant hydrolysis of the resulting imine to a carbonyl group, and finally, (c) intramolecular condensation of the amino group with the carbonyl group at the 2-position in the quinazolinone ring – the yield of the final product can be regarded as excellent.

Cyclization at the 2-position could also be achieved by varying the reducing agent. Thus, when quinazolinone **5e** was treated with sodium borohydride at room temperature, only the tetracyclic product **12** (Scheme 5), resulting from the addition of the secondary amino function onto the cyano group, was isolated in 90% yield. Further *N*-debenzylation under standard conditions provided the quinazolino[2,1-*b*]quinazoline derivative **13** in 67% yield. Unexpectedly, though, when the reduction of compound **12** was carried out with lithium tetrahydridoaluminate, compound **14**, resulting from the reduction of the carbonyl group, was obtained in 72% yield. A similar result was obtained when the quinazolinone **5e** was used under similar reducing conditions. Unambiguous structural characterization of compound **14** was achieved by X-ray crystallographic analysis (Figure 2).

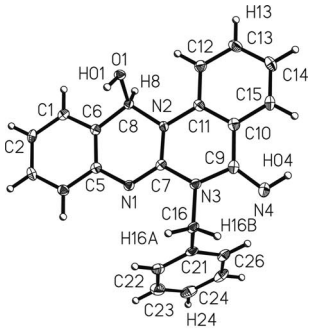
The 6,12-dehydro-5*H*-quinazolino[3,2-*a*]quinazoline **14** is nearly planar (the mean deviation from planarity of all its atoms is 0.057 Å). The phenyl ring is rotated by 109.7° with respect to the quinazoline ring. These molecules are interlinked by C13–H13···O1, C16–H16A···O1 and O1–H01···N1 hydrogen bonds, forming ribbons parallel to the *c* axis (Table 6).

Likewise, compound **5f** provided an interesting example of annulation at the 4-position in the quinazolinone ring. Catalytic hydrogenation of compound **5f** with Pd/C (Scheme 6) afforded an 80% yield of the diamino-substituted quinazolinone **15**, which on treatment with phosphorus pentachloride underwent cyclization to give the benzimidazo[1,2-*c*]quinazoline derivative **16** in 78% yield.

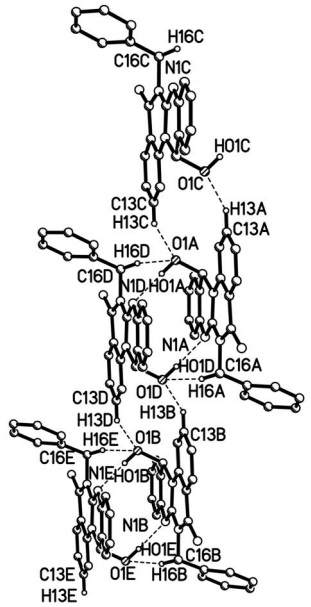
Although the 4*H*-3,1-benzoxazine ring system displays important biological activity, and a wide variety of derivatives of this ring system have been used as fungicidal and anti-inflammatory agents, as ostheoclasis inhibitors, as antirheumatics and as DNA-binding antitumour agents,[19] only a limited number of methods for the preparation of 4-alkylidene-4*H*-3,1-benzoxazines have been reported. A very recent approach involves the palladium-catalysed cyclization/alkoxycarbonylation of various substituted 2-[(trimethylsilyl)ethynyl]aniline amide or urea derivatives.[20]



Scheme 5. Preparation of quinazolino[2,1-*b*]quinazolines **11**–**14**. Reagents and conditions: (a) HCOOH, MeOH, Pd/C (80%); (b) $NaBH_4$, THF, room temp. (90%); (c) H_2/Pd/C (67%); (d) $LiAlH_4$, THF, 0 °C → room temp. (75%).



(a)



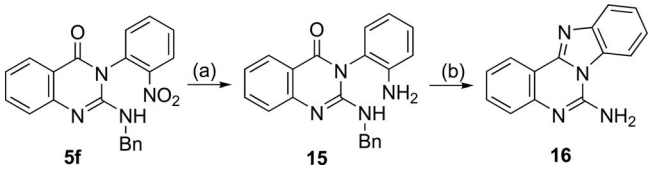
(b)

Figure 2. (a) ORTEP view of the molecular structure of **14** showing the atom labelling. (b) View of some of the hydrogen bonds in compound **14**.

Table 6. Hydrogen bonds [Å, °] in **14**.[a]

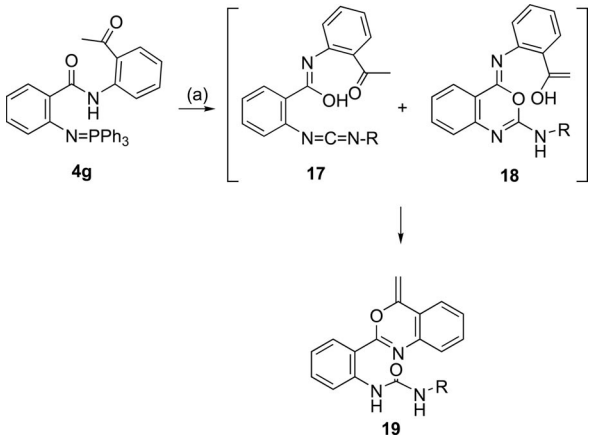
D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)
C(13)–H(13)···O(1)#1	0.95	2.57	3.291(2)	133.1
C(16)–H(16A)···O(1)#2	0.99	2.49	3.451(2)	163.3
O(1)–H(01)···N(1)#2	0.89(3)	1.89(3)	2.777(2)	174(3)
C(24)–H(24)···N(4)#3	0.95	2.61	3.414(3)	142.1

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x$, $-y + 1$, $-z + 1$; #2: $-x$, $-y + 1$, $-z + 2$; #3: $x + 1$, $-y + 3/2$, $z + 1/2$.



Scheme 6. Preparation of the benzimidazo[1,2-*c*]quinazoline **16**. Reagents and conditions: (a) H_2/Pd/C, THF, room temp., 80%; (b) PCl_5, toluene reflux, 78%.

Here we wish to report a one-pot procedure for the preparation of the otherwise not readily available 4-methylene-4*H*-3,1-benzoxazines **19** (Scheme 7) from the readily prepared iminophosphorane **4g**. Compound **4g** was prepared by the following two-step procedure: (a) acylation of 2-aminoacetophenone with *o*-azidobenzoyl chloride to give *N*-(2-acetylphenyl)-2-azidobenzamide in 77% yield, and (b) Staudinger reaction between this azide and triphenylphosphane to give the iminophosphorane **4g** in 99% yield.



Scheme 7. Preparation of 2-aryl-4-methylene-4*H*-3,1-benzoxazines **19**. Reagents and conditions: (a) RNCO, toluene, 1h, room temp. → reflux, 6–14 h.

When iminophosphorane **4g** was treated with alkyl or aryl isocyanates in dry toluene, first at room temperature and then with heating at reflux temperature, the previously unreported 2-aryl-4-methylene-4*H*-3,1-benzoxazines **19** were obtained as the only reaction products in yields ranging from 75 to 88%[21] (Table 7).

Table 7. Compounds **19** prepared.

Compound	R	Yield (%)
19a	Et	85
19b	Pr	78
19c	Ph	80
19d	4-$CH_3OC_6H_4$	75
19e	Bn	85
19f	4-$CH_3OC_6H_4CH_2$	88

The conversion of **4** into **19** can be explained in terms of an initial aza-Wittig reaction between the iminophosphorane **4g** and the isocyanate to give the carbodiimide **17** as a highly reactive intermediate that easily undergoes ring closure through nucleophilic attack of the hard end of the carboxamide group (the oxygen atom) on the hard electrophilic sp-hybridized carbon atom of the carbodiimide moiety to give the 4-imino-4*H*-3,1-benzoxazine ring **18**. Although it is well known that the isomerization of the iminobenzoxazine ring to a quinazolinone ring takes place under relatively mild conditions,[22] in this sequence the intermediate iminobenzoxazine **18** undergoes an unprecedented ring interconversion through nucleophilic attack of the enol form of the acetyl group at the 4-position in **18** to afford the new 2-aryl-4-methylene-4*H*-3,1-benzoxazine ureas **19**,

instead of the expected quinazolinone derivative. This conversion represents the first example of a rearrangement from an iminobenzoxazine to a methylenebenzoxazine (Scheme 7).

As a representative case, the structure of the 2-aryl-4-methylene-4*H*-3,1-benzoxazine **19e** was confirmed by X-ray analysis (Figure 3).

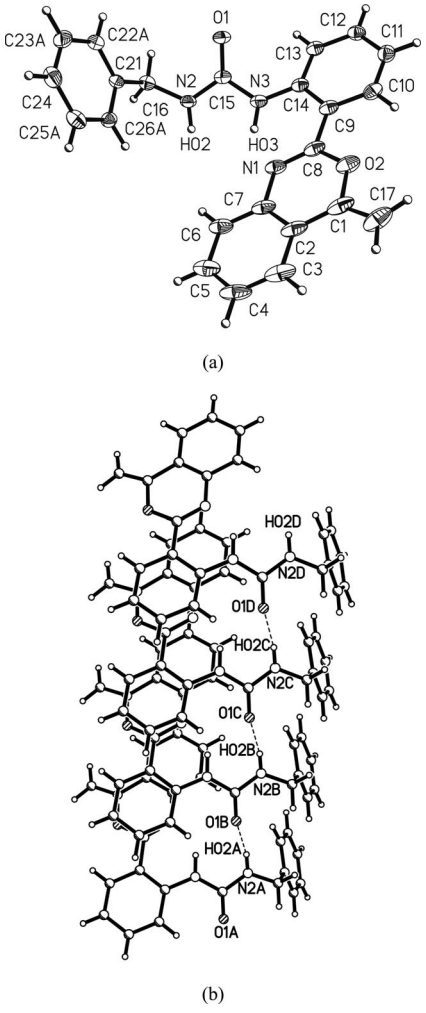


Figure 3. (a) ORTEP view of the molecular structure of **19e** showing the atom labelling. (b) View of some of the hydrogen bonds in compound **19e**.

The 2-aryl-4-methylene-4*H*-3,1-benzoxazine **19e** is almost planar (the mean deviation from planarity is 0.044Å, but is rotated by 41.7° with respect to the mean plane of the urea atoms). An intermolecular N–H···O hydrogen bond between the NH group and the oxygen atom of the urea is observed in the compound, linking the molecules in a chain parallel to the *a* axis (Table 8).

Table 8. Hydrogen bonds [Å, °] in **19e**.[a]

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)
N(2)–H(02)···O(1)#1	0.884(16)	1.985(16)	2.8354(14)	160.8(13)

[a] Symmetry transformations used to generate equivalent atoms: #1: $x - 1$, y, z.

Conclusions

We have developed an efficient route to fused quinazolines by using (arylimino)phosphoranes bearing *N*-(*o*-substituted-aryl)carboxamide substituents at their *ortho* positions. Aza-Wittig reactions between iminophosphoranes **4a**–**d**, each bearing a bromine group in the *N*-aryl substituent, and benzyl isocyanate or carbon disulfide provided the expected 2-(benzylamino)quinazolinones **5** and 2-mercaptoquinazolinones **9**, respectively. Similarly, and under appropriate reaction conditions, 4*H*-3,1-benzoxazine-4-imines **6** were isolated and characterized. The formation of quinazolinones **5** and **9** involves initial formation of a carbodiimide or an isothiocyanate as a highly reactive intermediate that undergoes cyclization through nucleophilic attack of the N–H group of the carboxamide on the central carbon atom of the heterocumulene moiety, whereas the formation of **6** could be explained by heterocyclization through the hard end of the carboxamide unit (oxygen atom).

Cu^{I}-catalysed *N*- and *S*-arylation of quinazolinones **5** and **9** afforded the expected fused ring systems: the benzimidazo[2,1-*b*]quinazolinones **8** and the benzothiazolo[2,3-*b*]-quinazolinones **10**. Reduction of the cyano functionality of quinazolinone **5e**, available through the aza-Wittig reaction between iminophosphorane **4e** (R^1 = CN, R^2 = R^3 = H) and benzyl isocyanate, with different reducing agents (Pd/C/formic acid, $NaBH_4$, $LiAlH_4$) yielded derivatives of the quinazolino[2,1-*b*]quinazoline ring system.

Treatment of iminophosphorane **4g**, derived from *N*-(2-acetylphenyl)-2-azidobenzamide, with aliphatic and aromatic isocyanates gave 4-methylene-*4H*-3,1-benzoxazines **18**. This transformation involves a novel aza-Wittig/carbodiimide ring closure/enol-induced rearrangement of a 4-imino-3,1-benzoxazine to afford a 4-methylene-3,1-benzoxazine.

Experimental Section

General Methods: All reactions were carried out under N_2, and the solvents were dried by standard procedures. Column chromatography was performed on silica gel (60 Å, 70–200 μm, SDS) as stationary phase. All melting points were determined with a hot-plate melting point apparatus and are uncorrected. IR spectra were recorded with a Nicolet 380 FT-IR instrument. NMR spectra (Bruker Avance 300 MHz, 400 MHz and 600 MHz) were determined with tetramethylsilane as an internal standard. The proton (^{1}H NMR) and carbon (^{13}C NMR) signals were assigned by DEPT or two-dimensional NMR experiments. Mass spectra were recorded with Agilent 5973 (EI), Agilent VL (ESI) and HPLC/MS TOF 6220 mass spectrometers. Elemental analyses were performed with a Carlo Erba EA-1108 elemental analyser.

2-Azido-*N*-arylbenzamides (3): A solution of an *o*-azidoaroyl chloride **1** (20 mmol) in anhydrous CH_2Cl_2 (2 mL) was added dropwise at 0 °C under nitrogen to a solution of an amino compound **2**

(20 mmol) in dry pyridine (15 mL). The resultant mixture was stirred at room temperature for 1 h. Afterwards, the mixture was poured into ice/H_2O (200 mL) to give a solid that was purified by column chromatography on silica gel with EtOAc/*n*-hexane (6:4) as eluent to provide a 2-azido-*N*-arylbenzamide **3**.

2-Azido-*N*-(2-bromophenyl)benzamide (3a): This compound (5.71 g, 90%) was obtained as white prisms, m.p. 120.5–121.5 °C (CH_2Cl_2/*n*-hexane, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.98 (br. s, 1 H), 8.57 (dd, *J* = 8.3, 1.5 Hz, 1 H), 8.27 (dd, *J* = 7.9, 1.6 Hz, 1 H), 7.59 (dd, *J* = 8.0, 1.5 Hz, 1 H), 7.56 (ddd, *J* = 8.0, 7.4, 1.6 Hz, 1 H), 7.35 (ddd, *J* = 8.3, 7.4, 1.5 Hz, 1 H), 7.30 (ddd, *J* = 7.91, 7.4, 1.0 Hz, 1 H), 7.26 (dd, *J* = 8.0, 1.0 Hz, 1 H), 7.0 (ddd, *J* = 8.0, 7.4, 1.5 Hz, 1 H, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 162.5, 137.0, 136.5, 133.0, 132.7, 132.4, 128.3, 125.3, 125.2, 124.8, 122.5, 118.6, 113.7 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3281, 2140, 1675, 1585, 1540, 751 cm^{-1}. MS (EI): *m*/*z* (%) = 318 (7) $[M + 2]^+$, 316 (7), 290 (19) $[M + 2 - N_2]^+$, 288 (17) $[M - N_2]^+$, 237 (40), 209 (99), 181 (71), 152 (44), 90 (100). $C_{13}H_9BrN_4O$ (317.14): calcd. C 49.23, H 2.86, N 17.67; found C 49.15, H 2.82, N 17.61.

2-Azido-*N*-(2,4-dibromophenyl)benzamide (3b): This compound (5.94 g, 75%) was obtained as white prisms, m.p. 115.5–116.2 °C (CH_2Cl_2/*n*-hexane, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 10.04 (br. s, 1 H), 8.50 (d, *J* = 8.9 Hz, 1 H), 8.27 (dd, *J* = 7.9, 1.46 Hz, 1 H), 7.73 (d, *J* = 2.3 Hz, 1 H), 7.57 (ddd, *J* = 8.0, 7.3, 1.7 Hz, 1 H), 7.46 (ddd, *J* = 8.9, 2.3, 0.4 Hz, 1 H), 7.30 (ddd, *J* = 7.9, 7.4, 1.1 Hz, 1 H), 7.26 (ddd, *J* = 8.0, 1.1, 0.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 162.5, 137.0, 135.8, 134.6, 133.2, 132.8, 131.2, 125.4, 124.4, 123.4, 118.6, 116.7, 114.0 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3300, 2136, 1676, 1585, 1523, 1304, 746 cm^{-1}. MS (EI): *m*/*z* (%) = 396 (5) $[M + 2]^+$, 394 (3) $[M]^+$, 368 (9) $[M - N_2]^+$, 289 (30), 287 (32), 120 (79), 92 (30), 90 (100). $C_{13}H_8Br_2N_4O$ (396.04): calcd. C 39.43, H 2.04, N 14.15; found C 39.38, H 2.01, N 14.09.

2-Azido-*N*-(2-bromo-4-fluorophenyl)benzamide (3c): This compound (5.76 g, 86%) was obtained as white prisms, m.p. 139–140 °C (CH_2Cl_2/*n*-hexane, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.85 (br. s, 1 H), 8.44 (dd, *J* = 9.2, 5.6 Hz, 1 H), 8.20 (dd, *J* = 7.4,1.6 Hz, 1 H), 7.50 (ddd, *J* = 8.0, 7.5, 1.6 Hz, 1 H), 7.27 (dd, *J* = 7.8, 2.9 Hz, 1 H), 7.23 (ddd, *J* = 7.9, 7.5, 1.0 Hz, 1 H), 7.20 (dd, *J* = 8.0, 1.0 Hz, 1 H), 7.01 (ddd, *J* = 9.2, 7.9, 2.9 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 162.5, 158.5 (d, $^1J_{C,F}$ = 248.4 Hz), 137.0, 133.1,133.0 (d, $^4J_{C,F}$ = 3.0 Hz), 132.7, 125.4, 124.5, 123.6 (d, $^3J_{C,F}$ = 8.1 Hz), 119.5 (d, $^2J_{C,F}$ = 25.7 Hz), 118.6 (C-6), 115.1 (d, $^2J_{C,F}$ = 21.8 Hz), 113.9 (d, $^3J_{C,F}$ = 9.4 Hz) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3294, 2132, 1670, 1596, 1539, 1482, 892, 854, 746 cm^{-1}. MS (EI): *m*/*z* (%) = 336 (5) $[M + 2]^+$, 334 (5) $[M]^+$, 308 (9) $[M + 2 - N_2]^+$, 306 (8) $[M - N_2]^+$, 289 (30), 287 (32), 227 (69), 199 (35), 146 (28), 120 (35), 90 (100). $C_{13}H_8BrFN_4O$ (335.13): calcd. C 46.59, H 2.41, N 16.72; found C 46.52, H 2.48, N 16.67.

2-Azido-*N*-(2-bromo-5-nitrophenyl)benzamide (3d): This compound (6.15 g, 85%) was obtained as white prisms, m.p. 173–174 °C (CH_2Cl_2/*n*-hexane, 4:1). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 10.26 (br. s, 1 H), 9.44 (d, *J* = 2.6 Hz, 1 H), 8.25 (dd, *J* = 8.0, 1.5 Hz, 1 H, 1 H), 7.79 (dd, *J* = 8.8, 2.6 Hz, 1 H), 7.69 (d, *J* = 8.8 Hz, 1 H), 7.55 (ddd, *J* = 8.0, 7.4, 1.5 Hz, 1 H), 7.27 (ddd, *J* = 8.0, 7.4, 1.1 Hz, 1 H), 7.22 (dd, *J* = 8.0, 1.1 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 162.7, 147.7, 137.7, 137.1, 133.7, 133.0, 132.9, 125.6, 123.7, 119.9, 119.2, 118.7, 116.9 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3261, 2127, 1669, 1532, 1516, 1474, 1310, 757 cm^{-1}. MS (EI): *m*/*z* (%) = 363 (5) $[M + 2]^+$, 361 (5) $[M]^+$, 335 (17) $[M + 2 - N_2]^+$, 333 (15) $[M - N_2]^+$, 254 (81), 208 (67), 120 (100), 90 (55). $C_{13}H_8BrN_5O_3$ (362.14): calcd. C 43.12, H 2.23, N 19.34; found C 43.05, H 2.27, N 19.28.

2-Azido-*N*-(2-cyanophenyl)benzamide (3e): This compound (4.1 g, 78%) was obtained as white prisms, m.p. 137–138 °C (CH_2Cl_2/*n*-hexane, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 10.55 (br. s, 1 H), 8.67 (dd, *J* = 9.1, 1.1 Hz, 1 H), 8.31 (ddd, *J* = 8.0, 1.7, 0.4 Hz, 1 H), 7.63 (dd, *J* = 7.9, 1.6 Hz, 1 H), 7.62 (ddd, *J* = 9.1, 7.4, 1.6 Hz, 1 H), 7.59 (ddd, *J* = 8, 7.4, 1.7 Hz,1 H), 7.32 (ddd, *J* = 8.0, 7.4, 1.1 Hz, 1 H), 7.19 (ddd, *J* = 7.9, 7.4, 1.1 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 162.7, 141.6, 137.5, 134.2, 133.6, 132.8, 132.3, 125.3, 124.0, 127.3, 121.2, 118.7, 117.1 102.3 ppm. IR (Nujol): $\tilde{\nu}$ = 2216, 2156, 1694, 1586, 1538, 1376, 1316, 746 cm^{-1}. MS (FAB positive): *m*/*z* (%) = 286 (100) $[M + Na]^+$, 258 (94), 236 (54), 170, 1 (50), 152, 1 (19), 150.1 (57). $C_{14}H_9N_5O$ (263.25): calcd. C 63.87, H 3.45, N 26.60; found C 63.81, H 3.40, N 26.52.

2-Azido-*N*-(2-nitrophenyl)benzamide (3f): This compound (4.81 g, 85%) was obtained as white prisms, m.p. 154–155 °C (CH_2Cl_2/*n*-hexane, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 11.69 (br. s, 1 H), 9.39 (dd, *J* = 8.6, 1.3 Hz, 1 H), 8.23 (dd, *J* = 8.4, 1.6 Hz, 1 H), 8.15 (dd, *J* = 8.2, 1.6 Hz, 1 H), 7.70–7.66 (m, 1 H), 7.58 (ddd, *J* = 8.0, 7.4, 1.60 Hz, 1 H), 7.31–7.27 (m, 2 H), 7.23 (ddd, *J* = 8.4, 7.3, 1.3 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 163.7, 137.7, 137.6, 135.4, 134.4, 133.3, 132.4, 125.8, 125.2, 125.0, 123.6, 123.3, 118.8 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3254, 2141, 1667, 1589, 1507, 1343, 1305, 1276, 738 cm^{-1}. MS (EI): *m*/*z* (%) = 283 (5) $[M]^+$, 255 (23) $[M - N_2]^+$, 179 (18), 140 (23), 121 (46), 90 (100). $C_{13}H_9N_5O_3$ (283.24): calcd. C 55.13, H 3.20, N 24.73; found C 55.08, H 3.27, N 24.65.

***N*-(2-Acetylphenyl)-2-azidobenzamide (3g):** This compound (4.31 g, 77%) was obtained as white prisms, m.p. 156–157 °C (CH_2Cl_2/*n*-hexane, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 12.25 (s, 1 H), 8.82 (dd, *J* = 8.5, 1.0 Hz, 1 H), 7.84 (dd, *J* = 8.0, 1.5 Hz, 1 H), 7.80 (dd, *J* = 8.0, 1.6 Hz, 1 H), 7.52 (ddd, *J* = 8.5, 7.5, 1.5 Hz, 1 H), 7.44 (ddd, *J* = 8.2, 7.3, 1.6 Hz, 1 H), 7.20–7.14 (m, 2 H), 7.09 (ddd, *J* = 8.0, 7.5, 1.0 Hz, 1 H), 2.60 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 202.2, 164.9, 140.3, 137.6, 134.9, 132.2, 131.5, 130.9, 127.6, 125.0, 123.0, 122.8, 121.5, 119.1, 28.6 ppm. IR (Nujol): $\tilde{\nu}$ = 3164, 2137, 1660, 1583, 1537, 1322, 1260, 749 cm^{-1}. MS (ESI): *m*/*z* (%) = 282 (23) $[M + 2]^+$, 281 (100) $[M + 1]^+$, 280 (14) $[M]^+$, 254 (17), 253 (42), 252 (24), 211 (42), 136 (45), 120 (43). $C_{15}H_{12}N_4O_2$ (280.28): calcd. C 64.28, H, 4.32; N, 19.99; found C 64.22, H 4.37, N 19.92.

***N*-Aryl-2-[(triphenylphosphoranylidene)amino]benzamides (4):** Triphenylphosphane (13.6 mmol) in CH_2Cl_2 (70 mL) was added dropwise at 0 °C under nitrogen to a solution of the appropriate 2-azido-*N*-arylbenzamide **3** (12 mmol) in anhydrous CH_2Cl_2 (70 mL). The resultant mixture was stirred at 0 °C for 1 h and then at room temperature for 12 h. Afterwards, the solvent was removed under reduced pressure, and the residue was crystallized from CH_2Cl_2/hexane (1:1) to give the iminophosphorane **4** in quantitative yield.

***N*-(2-Bromophenyl)-2-[(triphenylphosphoranylidene)amino]benzamide (4a):** This compound (6.47 g, 98%) was obtained as yellow prisms, m.p. 212–214 °C (CH_2Cl_2/*n*-hexane, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 13.07 (s, 1 H), 8.28 (dt, *J* = 7.9, 2.2 Hz, 1 H), 8.26 (dd, *J* = 7.8, 1.5 Hz, 1 H), 7.77–7.71 (m, 6 H), 7.57–7.52 (m, 3 H), 7.44–7.40 (m, 7 H), 7.35–7.31 (m,1 H), 6.97–6.92 (m, 2 H), 6.77 (ddd, *J* = 7.9, 7.3, 1.1 Hz, 1 H), 6.49 (d, *J* = 8.11 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 166.5 (d, ^4J = 1.5 Hz), 150.2 (d, ^2J = 2.6 Hz), 137.4, 132.6 (d, ^2J = 9.8 Hz), 132.3 (d, ^4J = 2.8 Hz), 132.2, 131.6 (d, ^3J = 3.3 Hz), 131.4, 129.2 (d, ^1J = 102.2 Hz), 128.9 (d, ^3J = 12.2 Hz), 127.5, 125.7, 125.3 (d, ^3J = 20.2 Hz), 124.9, 122.4 (d, ^4J = 12.2 Hz), 117.6, 116.2 ppm.

^{31}P NMR (125 MHz, $CDCl_3$, 25 °C): δ = 10.45 ppm. MS (EI): *m*/*z* (%) = 552 (31) (31) $[M + 2]^+$, 551.0 (23) $[M + 1]^+$, 550.0 (44) $[M]^+$, 471.0 (54), 380.0 (100), 352 (28), 262 (30), 201 (61), 183 (90), 152 (50), 108 (77), 91 (71). $C_{31}H_{24}BrN_2OP$ (551.41): calcd. C 67.52, H 4.39, N 5.08; found C 67.45, H 4.43, N 5.02.

***N*-(2,4-Dibromophenyl)-2-[(triphenylphosphoranylidene)amino]benzamide (4b):** This compound (7.33 g, 97%) was obtained as yellow prisms, m.p. 239–240 °C (CH_2Cl_2/*n*-hexane 4:1). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 13.11 (s, 1 H), 8.20 (dt, *J* = 7.9, 2.2 Hz, 1 H), 8.14 (d, *J* = 8.8 Hz, 1 H), 7.69–7.64 (m, 6 H), 7.53–7.48 (m, 3 H), 7.46 (d, *J* = 2.3 Hz, 1 H), 7.40–7.35 (m, 7 H), 6.89 (ddd, *J* = 8.1, 7.2, 2.2 Hz, 1 H), 6.71 (ddd, *J* = 7.9, 7.2, 1.1 Hz, 1 H), 6.43 (dt, *J* = 8.1, 1.1 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 166.5 (d, ^4J = 1.7 Hz), 150.3 (d, ^2J = 2.8 Hz), 136.7, 134.2, 133.6 (d, ^2J = 12.1 Hz), 132.4 (d, ^4J = 2.8 Hz), 131.6 (d, ^3J = 3.0 Hz), 131.6, 130.5, 129.0 (d, ^1J = 100.5 Hz), 128.9 (d, ^3J = 12.2 Hz), 126.6, 124.8 (d, ^3J = 20.8 Hz), 122.4 (d, ^4J = 12.5 Hz), 117.7, 116.5, 116.3 ppm. ^{31}P NMR (125 MHz, $CDCl_3$, 25 °C): δ = 11.05 ppm. MS (EI): *m*/*z* (%) = 630 (3) $[M + 2]^+$, 628 (2) $[M]^+$, 381 (27), 380 (100), 201 (44), 183 (67), 108. (21), 77 (15). $C_{31}H_{23}Br_2N_2OP$ (630.31): calcd. C 59.07, H 3.68, N 4.44; found C 59.01, H 3.72, N 4.38.

***N*-(2-Bromo-4-fluorophenyl)-2-[(triphenylphosphoranylidene)amino]-benzamide (4c):** This compound (6.56 g, 96%) was obtained as yellow prisms, m.p. 134–136 °C (CH_2Cl_2/*n*-hexane, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 13.17 (s, 1 H), 8.28 (dt, *J* = 7.9, 2.0 Hz, 1 H), 8.16 (dd, *J* = 9.0, 5.8 Hz, 1 H), 7.77–7.70 (m, 6 H), 7.58–7.54 (m, 3 H), 7.45–7.41 (m, 6 H), 7.15 (dd, *J* = 8.1, 2.9 Hz, 1 H), 7.06 (ddd, *J* = 9.0, 8.0, 2.9 Hz, 1 H), 6.96 (ddd, *J* = 8.1, 7.1, 2.0 Hz, 1 H), 6.78 (ddd, *J* = 8.1, 7.9, 1.0 Hz, 1 H), 6.49 (dt, *J* = 7.1, 1.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 166.5 (d, ^4J = 1.9 Hz), 158.6 (d, $^1J_{C,F}$ = 246.7 Hz), 150.2 (d, ^2J = 2.8 Hz), 133.1 (d, $^4J_{C,F}$ = 2.8 Hz), 132.6 (d, ^2J = 9.8 Hz), 132.3 (d, ^4J = 2.9 Hz), 131.6 (d, ^3J = 2.4 Hz), 131.5, 129.0 (d, ^1J = 100.3 Hz), 128.9 (d, ^3J = 12.1 Hz), 126.3 (d, $^3J_{C,F}$ = 8.4 Hz), 124.9 (d, ^3J = 20.5 Hz), 122.5 (d, ^4J = 12.1 Hz), 119.0 (d, $^2J_{C,F}$ = 25.0 Hz), 117.7, 116.2 (d, $^3J_{C,F}$ = 10.8 Hz), 114.4 (d, $^2J_{C,F}$ = 21.5 Hz) ppm. ^{31}P NMR (125 MHz, $CDCl_3$, 25 °C): δ = 10.52 ppm. MS (EI): *m*/*z* (%) = 570 (30) $[M + 2]^+$, 569 (21) $[M + 1]^+$, 568 (40) $[M]^+$, 489 (54), 261 (26), 201 (64), 198 (98), 152 (49), 108 (100), 78 (47). $C_{31}H_{23}BrFN_2OP$ (569.40): calcd. C 65.39, H 4.07, N, 4.92; found C 65.32, H 4.24, N 4.85.

***N*-(2-Bromo-5-nitrophenyl)-2-[(triphenylphosphoranylidene)amino]-benzamide (4d):** This compound (6.87 g, 96%) was obtained as yellow prisms, m.p. 272–273 °C (CH_2Cl_2/*n*-hexane, 4:1). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 13.53 (s, 1 H), 9.21 (d, *J* = 3.3 Hz, 1 H), 8.28 (dt, *J* = 7.9, 2.0 Hz, 1 H), 7.78–7.69 (m, 7 H), 7.60–7.54 (m, 3 H), 7.52 (d, *J* = 8.8 Hz, 1 H), 7.48–7.42 (m, 6 H), 6.98 (ddd, *J* = 8.1, 7.2, 2.0 Hz, 1 H), 6.79 (ddd, *J* = 7.9, 7.2, 1.1 Hz, 1 H), 6.50 (d, *J* = 8.1 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 166.8 (d, ^4J = 1.5 Hz), 150.5 (d, ^2J = 3.0 Hz), 147.4, 138.8, 132.6 (d, ^2J = 9.9 Hz), 132.6, 132.5 (d, ^4J = 2.9 Hz), 132.0, 131.7 (d, ^3J = 2.3 Hz), 129.0 (d, ^3J = 12.2 Hz), 128.9 (d, ^1J = 100.5 Hz), 124.4 (d, ^3J = 20.6 Hz), 122.7, 122.5 (d, ^4J = 12.3 Hz), 120.0, 118.9, 117.9 ppm. ^{31}P NMR (125 MHz, $CDCl_3$, 25 °C): δ = 11.71 ppm. MS (EI): *m*/*z* (%) =597 (7) $[M + 2]^+$, 595 (7) $[M]^+$, 381 (29), 380 (100), 201 (62), 183 (95), 108 (15), 90 (17). $C_{31}H_{23}BrN_3O_3P$ (596.41): calcd. C 62.43, H 3.89, N 7.05; found C 62.35, H 3.93, N 7.01.

***N*-(2-Cyanophenyl)-2-[(triphenylphosphoranylidene)amino]benzamide (4e):** This compound (5.67 g, 95%) was obtained as yellow prisms, m.p. 206–208 °C (CH_2Cl_2/*n*-hexane, 4:1). ^{1}H NMR (400 MHz, $[D_6]$DMSO, 25 °C): δ = 13.90 (s, 1 H), 8.06–8.02 (m, 2 H), 7.78 (dd, *J* = 12.2, 7.3 Hz, 6 H), 7.71–7.61 (m, 5 H), 7.50 (dt, *J* = 7.6, 3.0 Hz, 6 H, 6 H), 7.27 (t, *J* = 7.6 Hz, 1 H), 7.0 (dt, *J* = 7.6, 1.7 Hz, 1 H), 6.72 (t, *J* = 7.4 Hz, 1 H), 6.47 (d, *J* = 8.1 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $[D_6]$DMSO, 25 °C): δ = 165.4, 150.3 (d, ^2J = 2.6 Hz), 141.0, 133.6, 132.8 (d, ^4J = 2.7 Hz), 132.7, 132.3 (d, ^2J = 10.0 Hz), 132.1, 131.0 (d, ^4J = 2.4 Hz), 129.3 (d, ^3J = 12.2 Hz), 127.9 (d, ^1J = 100.1 Hz), 124.7, 124.6, 123.5 (d, ^3J = 20.4 Hz), 122.2 (d, ^3J = 12.5 Hz), 117.5, 116.7, 105.3 ppm. ^{31}P NMR (125 MHz, $CDCl_3$, 25 °C): δ = 12.38 ppm. MS (ESI): *m*/*z* (%) =500 (30) $[M + 3]^+$, 499 (61) $[M + 2]^+$, 498 (11) $[M + 1]^+$, 381 (18), 380 (90), 279 (100), 221 (17), 218 (20). $C_{32}H_{24}N_3OP$ (497.53): calcd. C 77.25, H 4.86, N 8.45; found C 77.20, H 4.92, N 8.37.

***N*-(2-Nitrophenyl)-2-[(triphenylphosphoranylidene)amino]benzamide (4f):** This compound (6.02 g, 97%) was obtained as yellow prisms, m.p. 173–175 °C (CH_2Cl_2/*n*-hexane, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 13.81 (s, 1 H), 8.51 (dd, *J* = 8.4, 1.2 Hz, 1 H), 8.19 (dt, *J* = 7.9, 1.3 Hz, 1 H), 7.99 (dd, *J* = 8.4, 1.5 Hz, 1 H), 7.80–7.74 (m, 6 H), 7.60 (ddd, *J* = 8.4, 7.3, 1.5 Hz, 1 H), 7.55–7.51 (m, 3 H), 7.43–7.39 (m, 6 H), 7.14 (ddd, *J* = 8.4, 7.3, 1.2 Hz, 1 H), 6.98 (ddd, *J* = 8.0, 7.5, 1.3 Hz, 1 H), 6.76 (ddd, *J* = 7.9, 7.5, 0.9 Hz, 1 H), 6.50 (d, *J* = 8.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 167.1 (d, ^4J = 1.8 Hz), 150.5, 139.3, 134.5, 134.1, 132.5 (d, ^2J = 9.9 Hz), 132.2 (d, ^4J = 3.0 Hz), 131.9, 131.7 (d, ^3J = 2.5 Hz), 129.0 (d, ^1J = 100.9 Hz), 128.9 (d, ^3J = 12.3 Hz), 128.5, 125.2, 125.0 (d, ^3J = 21.2 Hz), 123.0, 122.5 (d, ^4J = 12.3 Hz), 117.6 ppm. ^{31}P NMR (125 MHz, $CDCl_3$, 25 °C): δ = 10.31 ppm. MS (EI): *m*/*z* (%) = 518 (8) $[M + 1]^+$, 517 (25) $[M]^+$, 380 (99), 380 (90), 277 (29), 201 (77), 183 (27) (100) 108, 77 (37). $C_{31}H_{24}N_3O_3P$ (517.51): calcd. C 71.95, H 4.67, N 8.12; found C 71.91, H 4.72, N 8.08.

***N*-(2-Acetylphenyl)-2-[(triphenylphosphoranylidene)amino]benzamide (4g):** This compound (5.92 g, 96%) was obtained as yellow prisms, m.p. 195–196 °C (CH_2Cl_2/*n*-hexane, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 13.40 (s, 1 H), 8.27 (dd, *J* = 8.3, 1.1 Hz, 1 H), 8.07 (dt, *J* = 7.8, 2.2 Hz, 1 H), 7.79–7.73 (m, 6 H), 7.62 (dd, *J* = 7.9, 1.5 Hz, 1 H), 7.51–7.43 (m, 4 H), 7.39–7.34 (m, 6 H), 7.08 (ddd, *J* = 7.9, 7.3,1.1 Hz, 1 H), 6.92 (ddd, *J* = 7.2, 8.1, 2.2 Hz, 1 H), 6.71 (ddd, *J* = 7.2, 7.8, 1.0 Hz, 1 H), 6.46 (dt, *J* = 8.1, 1.0 Hz, 1 H), 2.22 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 199.4, 167.5 (d, ^4J = 1.1 Hz), 150.0 (d, ^2J = 1.9 Hz), 138.6 132.8, 132.6 (d, ^2J = 9.7 Hz), 132.0 (d, ^4J = 2.9 Hz), 131.5 (d, ^4J = 2.8 Hz), 131.4, 129.8, 129.7 (d, ^1J = 100.7 Hz), 128.7 (d, ^3J = 12.4 Hz), 128.2, 126.7 (d, ^3J = 21.9 Hz), 123.9, 122.7, 122.4 (d, ^2J = 12.0 Hz), 117.3, 28.5 ppm. ^{31}P NMR (161.9 MHz, $CDCl_3$, 25 °C): δ = 7.73 ppm. MS (ESI): *m*/*z* (%) =516 (23) $[M + 2]^+$, 515 (100) $[M + 1]^+$. $C_{33}H_{27}N_2O_2P$ (514.55): calcd. C 77.03, H 5.20, N 5.44; found C 77.01, H 5.25, N 5.47.

3-Aryl-2-benzylamino-3*H*-quinazolin-4-ones (5). Method A: A mixture of the appropriate *N*-aryl-2-[(triphenylphosphoranylidene) amino]benzamide **4** (1.6 mmol) and benzyl isocyanate (0.43 g, 3.2 mmol) in anhydrous toluene (60 mL), was stirred at room temperature under nitrogen for 1 h and then was heated at reflux temperature for 6 h. Afterwards, the solvent was removed under reduced pressure, and the mixture was separated by column chromatography on silica gel with EtOAc/*n*-hexane (2:3) as eluent to provide 3-aryl-2-(benzylamino)-3*H*-quinazolin-4-ones **5** in 5–80% yields and 1-[4-(arylimino)-4*H*-benzo[*d*][1,3]oxazin-2-yl]-1,3-dibenzylureas **6** in 10–90% yields. **Method B:** A mixture of an *N*-aryl-2-[(triphenylphosphoranylidene)amino]benzamide **4** (0.45 mmol), benzyl isocyanate (0.54 mmol), and anhydrous *o*-xylene (5 mL) was introduced under nitrogen into a pressure vial

(10 mL) containing a magnetic stirrer bar. The vessel reaction was irradiated in a single-mode microwave (CEM Discover Focused Synthesizer) at 160 °C (by modulation of the power) for 15 min. The mixture was cooled rapidly to room temperature. Afterwards, the solvent was removed at reduced pressure, and the mixture was separated by column chromatography on silica gel with EtOAc/*n*-hexane (2:3) as eluent to provide 3-aryl-2-benzylamino-3*H*-quinazolin-4-ones **5** in 75–87% yields and 1-[4-(arylimino)-4*H*-benzo[*d*][1,3]oxazin-2-yl]-1,3-dibenzylureas **6** in 8–20% yields.

2-(Benzylamino)-3-(2-bromophenyl)-3*H*-quinazolin-4-one (5a): This compound (0.15 g, 80%) was obtained as white prisms, m.p. 147–150 °C (EtOAc/*n*-hexane, 2:3). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.08 (dd, *J* = 8.0, 1.3 Hz, 1 H), 7.72 (dd, *J* = 8.4, 1.4 Hz, 1 H), 7.57 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1 H), 7.44 (ddd, *J* = 8.0, 7.3, 1.4 Hz, 1 H), 7.39 (dd, *J* = 8.3, 0.5 Hz, 1 H), 7.34–7.30 (m, 2 H), 7.26–7.16 (m, 5 H), 7.13 (ddd, *J* = 8.0, 7.1, 0.5 Hz, 1 H), 4.70 (dd, *J* = 15.0, 5.8 Hz, 1 H), 4.55 (dd, *J* = 15.0, 5.3 Hz, 1 H), 4.16 (t, *J* = 5.4 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 161.9, 149.4, 148.5, 138.2, 134.8, 134.5, 134.1, 131.5, 130.8 (2 C), 129.5, 129.5 (2 C), 127.4 (3 C), 127.4, 125.2, 123.7, 122.8, 117.6, 45.6 ppm. MS (EI): *m*/*z* (%) = 407 (16) $[M + 2]^+$, 405 (17) $[M]^+$, 327 (58), 326 (100), 248 (74), 221 (51), 119 (74), 106 (45), 91 (75). $C_{21}H_{16}BrN_3O$ (406.28): calcd. C 62.08, H 3.97, N 10.34; found C 62.02, H 4.03, N 10.28.

2-(Benzylamino)-3-(2,4-dibromophenyl)-3*H*-quinazolin-4-one (5b): This compound (0.185 g, 85%) was obtained as white prisms, m.p. 134–136 °C (EtOAc/*n*-hexane, 2:3). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.14 (ddd, *J* = 8.0, 1.5, 0.5 Hz, 1 H), 7.95 (d, *J* = 2.1 Hz,1 H), 7.65 (ddd, *J* = 8.2, 7.1, 1.5 Hz, 1 H), 7.64 (dd, *J* = 8.4, 2.1 Hz, 1 H), 7.46 (dd, *J* = 8.2, 0.5 Hz, 1 H), 7.35–7.25 (m, 5 H), 7.25 (d, *J* = 8.4 Hz, 1 H), 7.21 (ddd, *J* = 8.0, 7.1, 1.1 Hz, 1 H), 4.77 (dd, *J* = 14.9, 5.9 Hz, 1 H), 4.62 (dd, *J* = 14.9, 5.3 Hz, 1 H), 4.20 (t, *J* = 5.4 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 161.7, 149.4, 148.1, 138.1, 137.1, 135.0, 133.3, 132.9, 131.9, 128.7 (2 C), 127.6 (3 C), 127.3, 125.2, 124.8, 124.7 (2 C), 123.0, 117.4, 45.7 ppm. MS (EI): *m*/*z* (%) = 487 (5) $[M + 4]^+$, 485 (10) $[M + 2]^+$, 483 (5) $[M]^+$, 406 (30), 404 (39), 326 (10), 119 (11), 106 (18), 91 (100). $C_{21}H_{15}Br_2N_3O$ (485.17): calcd. C 51.99, H 3.12, N 8.66; found C 51.93, H 3.18, N 8.61.

2-(Benzylamino)-3-(2-bromo-4-fluorophenyl)-3*H*-quinazolin-4-one (5c): This compound (0.16 g, 85%) was obtained as white prisms, m.p. 145–146 °C (EtOAc/*n*-hexane, 2:3). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.14 (dd, *J* = 7.9, 0.9 Hz, 1 H), 7.65 (ddd, *J* = 8.2, 7.0, 1.4 Hz,1 H), 7.54 (dd, *J* = 7.7, 2.7 Hz, 1 H), 7.46 (d, *J* = 8.2 Hz, 1 H), 7.37 (dd, *J* = 8.7, 5.4 Hz, 1 H), 7.31–7.13 (m, 7 H), 4.77 (dd, *J* = 14.9, 5.8 Hz, 1 H), 4.62 (dd, *J* = 14.9, 5.2 Hz, 1 H), 4.21 (t, *J* = 5.5 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 162.8 (d, $^1J_{C,F}$ = 225.6 Hz), 161.9, 149.4, 148.4, 138.1, 135.0, 131.9 (d, $^3J_{C,F}$ = 9.2 Hz), 130.3 (d, $^4J_{C,F}$ = 3.9 Hz), 128.7, 127.6, 127.5, 127.4, 125.2, 124.6 (d, $^3J_{C,F}$ = 10 Hz), 123, 122 (d, $^2J_{C,F}$ = 25.5 Hz), 117.5, 116.9 (d, $^2J_{C,F}$ = 22.6 Hz), 45.7 ppm. MS (EI): *m*/*z* (%) = 425 (10) $[M + 2]^+$, 423 (10) $[M]^+$, 344 (56), 319 (16), 266 (19), 239 (27), 235 (22), 133 (67), 132 (60), 106 (24), 105 (59), 104 (72), 91 (100). $C_{21}H_{15}BrFN_3O$ (423.04): calcd. C 59.45, H 3.56, N 9.90; found C 59.41, H 3.60, N 9.85.

2-(Benzylamino)-3-(2-bromo-5-nitrophenyl)-3*H*-quinazolin-4-one (5d): This compound (0.20 g, 75%) was obtained as white prisms, m.p. 191–193 °C (EtOAc/*n*-hexane, 2:3). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.26 (dd, *J* = 2.6, 0.4 Hz, 1 H), 8.23 (dd, *J* = 8.6, 2.6 Hz, 1 H), 8.13 (ddd, *J* = 7.9, 1.6, 0.4 Hz, 1 H), 7.99 (dd, *J* = 8.6, 0.4 Hz, 1 H), 7.68 (ddd, *J* = 8.3, 7.1,1.6 Hz, 1 H), 7.49 (dd, *J* = 8.3, 1.1 Hz, 1 H), 7.31–7.25 (m, 5 H), 7.24 (ddd, *J* = 7.9, 7.1, 1.1 Hz, 1 H), 4.82 (dd, *J* = 14.8, 6.0 Hz, 1 H), 4.59 (dd, *J* = 14.8, 5.0 Hz, 1 H), 4.13 (t, *J* = 5.5 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 161.7, 149.3, 148.2, 147.5, 137.8, 135.5, 135.4, 135.3, 131.9, 128.7, 127.7, 127.6, 127.3, 126.4, 126.0, 125.4, 123.3, 117.2, 45.8 ppm. MS (EI): *m*/*z* (%) = 452 (11) $[M + 2]^+$, 450 (10) $[M]^+$, 372 (47), 371 (100), 325 (40), 293 (17), 247 (14), 162 (19), 145 (15), 119 (29), 106 (47), 92 (22), 91 (87). $C_{21}H_{15}BrN_4O_3$ (451.27): calcd. C 55.89, H 3.35, N 12.42; found C 55.84, H 3.39, N 12.35.

2-(Benzylamino)-3-(2-cyanophenyl)-3*H*-quinazolin-4-one (5e): This compound (0.138 g, 87%) was obtained as white prisms, m.p. 207–209 °C (EtOAc/*n*-hexane, 3:2). ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 8.15 (dd, *J* = 8.0, 1.4 Hz, 1 H), 7.98–7.91 (m, 2 H), 7.79–7.75 (m, 2 H), 7.66–7.61 (m, 1 H), 7.32–7.26 (m, 5 H), 7.21–7.14 (m, 2 H), 6.86 (t, *J* = 6.0 Hz, 1 H), 4.60–4.49 (m, 2 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 162.0, 150.1, 149.7, 140.1, 138.0, 135.8, 135.4, 134.8, 131.4, 130.9 (2 C), 128.5, 127.2, 127.0, 126.9, 125.2, 122.6, 116.9, 116.3, 113.3, 44.5 ppm. IR (Nujol): $\tilde{\nu}$ = 3390, 2234, 1678, 1582, 770, 718, 694 cm^{-1}. MS (ESI): *m*/*z* (%) = 354 (22) $[M + 2]^+$, 353 (100) $[M + 1]^+$, 278 (23), 152 (23), 150 (78). $C_{22}H_{16}N_4O$ (352.39): calcd. C 74.98, H 4.58, N 15.90; found C 74.93, H 4.64, N 15.85.

2-(Benzylamino)-3-(2-nitrophenyl)-3*H*-quinazolin-4-one (5f): This compound (0.14 g, 85%) was obtained as white prisms, m.p. 145–149 °C (EtOAc/*n*-hexane, 2:3). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.15 (dd, *J* = 8.1, 1.4 Hz, 1 H), 8.01 (dd, *J* = 7.9, 1.2 Hz, 1 H), 7.74 (ddd, *J* = 7.8, 1.4 Hz, 1 H), 7.65–7.55 (m, 2 H), 7.40 (dd, *J* = 7.8, 1.1 Hz, 2 H), 7.26–7.11 (m, 6 H), 4.70 (dd, *J* = 5.7, 4.8 Hz, 1 H), 4.57 (dd, *J* = 5.2, 4.8 Hz, 1 H), 4.14 (t, *J* = 5.5 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 162.2, 149.3, 148.3, 146.9 (2 C), 138.1, 135.1 (2 C), 131.6, 131.2, 128.7, 127.6, 127.5, 127.2, 126.5, 125.3, 123.1, 117.3, 45.8 ppm. MS (EI): *m*/*z* (%) = 372 (4) $[M]^+$, 355.1 (47), 326.0 (47), 324 (26), 251 (19), 249 (32), 248 (68), 237 (35), 236 (30), 235 (60), 146 (30), 91 (100). $C_{21}H_{16}N_4O_3$ (372.38): calcd. C 67.73, H 4.33, N 15.05; found C 67.68, H 4.39, N 15.01.

1,3-Dibenzyl-1-{4-[(2-bromophenyl)imino]-4*H*-benzo[*d*][1,3]oxazin-2-yl}urea (6a): This compound (0.19 g, 79%) was obtained as white prisms, m.p. 115–119 °C (EtOAc/*n*-hexane, 2:3). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 10.53 (t, *J* = 5.3 Hz, 1 H), 8.10 (dd, *J* = 7.8, 1.5 Hz, 1 H), 7.56 (dd, *J* = 8.0, 1.2 Hz, 1 H), 7.46 (ddd, *J* = 7.8, 7.6, 1.5 Hz, 1 H), 7.34–7.30 (m, 4 H), 7.25–7.17 (m, 3 H), 7.08–7.01 (m, 4 H), 6.95 (ddd, *J* = 8.0, 7.8, 1.5 Hz, 1 H), 6.81 (dd, *J* = 7.9, 1.5 Hz, 1 H), 6.58 (d, *J* = 7.0 Hz, 2 H), 4.80 (br. s, 2 H), 4.56 (d, *J* = 5.3 Hz, 2 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 154.0, 150.2, 145.7, 144.7, 142.8, 138.3, 137.2, 134.5, 133.0, 128.7, 128.3, 128.0, 127.4, 127.4, 127.0, 127.0, 126.9, 126.3, 125.3, 124.1, 122.4, 115.7, 115.6, 46.1, 45.1 ppm. MS (ESI): *m*/*z* (%) = 542 (34) $[M + 4]^+$, 541 (47) $[M + 3]^+$, 540 (48) $[M + 2]^+$, 539 (100) $[M + 1]^+$, 538 (16) $[M]^+$, 408 (43), 407 (28), 406 (46), 301 (79), 299 (78), 235 (75). $C_{29}H_{23}BrN_4O_2$ (539.42): calcd. C 64.57, H 4.30, N 10.39; found C 64.52, H 4.37, N 10.33.

1,3-Dibenzyl-1-{4-[(2,4-dibromophenyl)imino]-4*H*-benzo[*d*][1,3]oxazin-2-yl}urea (6b): This compound (0.196 g, 70%) was obtained as white prisms, m.p. 140–142 (EtOAc/*n*-hexane, 2:3). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 10.48 (t, *J* = 5.2 Hz, 1 H), 8.08 (dd, *J* = 7.8, 1.2 Hz, 1 H), 7.63 (d, *J* = 2.1 Hz, 1 H), 7.49 (ddd, *J* = 7.9, 7.4, 1.2 Hz, 1 H), 7.33–7.31 (m, 4 H), 7.24–7.22 (m, 2 H), 7.21 (dd, *J* = 8.4, 2.1 Hz, 1 H), 7.11–7.10 (m, 3 H), 7.05 (d, *J* = 7.9 Hz, 1 H), 6.65–6.62 (m, 2 H), 6.58 (d, *J* = 8.4 Hz, 1 H), 4.82 (br. s, 2 H), 4.56 (d, *J* = 5.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 153.8, 150.0, 146.2, 143.8, 142.8, 138.3, 137.0, 135.0, 134.7, 131.0, 128.7, 128.4, 127.4, 127.4, 127.0, 126.9, 126.5, 125.9,

124.2, 123.3, 116.9, 116.7 (2 C), 115.3, 46.3, 45.1 ppm. MS (ESI): *m*/*z* (%) = 641 (36) $[M + 2 + Na]^+$, 639 (23) $[M + Na]^+$, 620 (43) $[M + 4]^+$, 619 (100) $[M + 3]^+$, 617 (37) $[M + 1]^+$, 488 (45), 486 (70), 484 (46), 330 (19), 279 (64). $C_{29}H_{22}Br_2N_4O_2$ (618.32): calcd. C 56.33, H 3.59, N 9.06; found C 56.28, H 3.64, N 8.97.

1,3-Dibenzyl-1-{4-[(2-bromo-4-fluorophenyl)imino]-4*H*-benzo[*d*][1,3]-oxazin-2-yl}urea (6c): This compound (0.225 g, 90%) was obtained as white prisms, m.p. 142–145 °C (EtOAc/*n*-hexane, 2:3). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 10.55 (t, *J* = 5.3 Hz, 1 H), 8.17 (dd, *J* = 7.9, 0.9 Hz, 1 H), 7.56 (ddd, *J* = 8.0, 7.4, 1.5 Hz, 1 H), 7.42–7.39 (m, 4 H), 7.38–7.28 (m, 3 H), 7.18–7.15 (m, 3 H), 7.11 (dd, *J* = 8.1, 0.5 Hz, 1 H), 6.94–6.92 (m, 1 H), 6.79–6.73 (m, 3 H), 4.90 (br. s, 2 H), 4.63 (d, *J* = 5.3 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 159.0 (d, $^1J_{C,F}$ = 247.8 Hz), 153.9, 150.1, 146.2, 142.8, 140.8 (d, $^4J_{C,F}$ = 3.2 Hz), 138.3, 137.1, 134.6, 128.7, 128.3, 127.4, 127.4, 127.0, 126.4, 126.2, 124.2, 122.7 (d, $^3J_{C,F}$ = 8.3 Hz), 119.9 (d, $^2J_{C,F}$ = 25.1 Hz), 115.7 (d, $^3J_{C,F}$ = 9.6 Hz), 115.5, 46.2, 45.1 ppm. MS (ESI): *m*/*z* (%) = 579 (100) $[M + Na]^+$, 559 (3) $[M + 3]^+$, 557 (5) $[M + 1]^+$, 448 (10). $C_{29}H_{22}BrFN_4O_2$ (557.1): calcd. C 62.49, H 3.98, N 10.05; found C 62.43, H 4.04, N 9.98.

1,3-Dibenzyl-1-{4-[(2-bromo-5-nitro-phenyl)imino]-4*H*-benzo[*d*][1,3]-oxazin-2-yl}urea (6d): This compound (39 mg, 15%) was obtained as white prisms, m.p. 155–159 °C (EtOAc/*n*-hexane, 2:3). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 10.48 (t, *J* = 5.3 Hz, 1 H), 8.17 (dd, *J* = 7.9, 1.2 Hz, 1 H), 7.81 (dd, *J* = 8.8, 2.6 Hz, 1 H), 7.72 (d, *J* = 8.8 Hz, 1 H), 7.65–7.59 (m, 2 H), 7.41–7.31 (m, 6 H), 7.16 (dd, *J* = 8.1, 0.5 Hz, 1 H), 7.08–7.05 (m, 3 H), 6.61 (dd, *J* = 7.2, 1.60 Hz, 2 H), 4.85 (br. s, 2 H), 4.62 (d, *J* = 5.3 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 153.6 149.8, 147.6, 147.4, 146.1, 143.0, 138.1, 136.7, 135.2, 133.4, 128.7, 128.6, 128.3, 127.4, 127.4, 127.2, 127.0, 125.4, 124.4, 122.9, 119.5, 117.1, 114.8, 46.4, 45.2 ppm. MS (ESI): *m*/*z* (%) = 606 (21) $[M + Na]^+$, 586 (37) $[M + 3]^+$, 584 (17) $[M + 1]^+$, 541 (33), 503 (72), 500 (84), 463 (46), 356 (37), 264 (30), 263 (100), 241 (56). $C_{29}H_{22}BrN_5O_4Br$ (584.42): calcd. C 59.60, H 3.79, N 11.98; found C 59.52, H 3.83, N 11.92.

1,3-Dibenzyl-1-{4-[(2-cyanophenyl)imino]-4*H*-benzo[*d*][1,3]oxazin-2-yl}urea (6e): This compound (22 mg, 10%) was obtained as white prisms, m.p. 145–146 °C (EtOAc/*n*-hexane, 2:3). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 10.53 (t, *J* = 5.3 Hz, 1 H), 8.19 (d, *J* = 7.7 Hz, 1 H), 7.62 (dd, *J* = 7.8, 0.9 Hz, 1 H), 7.59–7.56 (m, 1 H), 7.47–7.45 (m, 1 H), 7.42–7.39 (m, 4 H), 7.33–7.30 (m, 2 H), 7.21–7.18 (m, 1 H), 7.17–7.12 (m, 4 H), 6.92 (d, *J* = 8.1 Hz), 6.70 (d, *J* = 6.9 Hz, 2 H), 4.91 (br. s, 2 H), 4.64 (d, *J* = 5.3 Hz, 2 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 153.8, 149.8, 148.9, 146.8, 142.9, 138.2, 137.0, 135.0, 133.4, 133.0, 128.7, 128.4, 127.5, 127.4, 127.1, 126.6, 126.1, 124.3, 122.1, 117.0, 115.3, 105.7, 46.2, 45.2 ppm. MS (ESI): *m*/*z* (%) = 487 (17) $[M + 2]^+$, 486 (44) $[M + 1]^+$, 374 (18), 352 (26), 247 (26), 246 (85), 235 (51), 149 (83), 137 (37), 123 (56), 111 (62), 110 (100). $C_{30}H_{23}N_5O_2$ (485.54): calcd. C 74.21, H 4.77, N 14.42; found C 74.17, H 4.82, N 14.35.

1,3-Dibenzyl-1-{4-[(2-nitrophenyl)imino]-4*H*-benzo[*d*][1,3]oxazin-2-yl}urea (6f): This compound (0.128 g, 57%) was obtained as white prisms, m.p. 141–143 °C (EtOAc/*n*-hexane, 2:3). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 10.54 (t, *J* = 5.29 Hz, 1 H), 8.10 (dd, *J* = 7.9, 1.5 Hz, 1 H), 8.0 (dd, *J* = 8.3, 1.4 Hz, 1 H), 7.57 (ddd, *J* = 8.2, 7.6, 1.5 Hz, 1 H), 7.47 (ddd, *J* = 8.0, 7.5, 1.4 Hz, 1 H), 7.41–7.37 (m, 4 H), 7.34–7.28 (m, 2 H), 7.22 (ddd, *J* = 8.3, 7.5, 1.3 Hz, 1 H), 7.14–7.07 (m, 4 H), 6.88 (dd, *J* = 8.0, 1.3 Hz, 1 H), 6.65 (dd, *J* = 7.3, 1.2 Hz, 2 H), 4.82 (br. s, 2 H), 4.63 (d, *J* = 5.3 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 153.8, 149.9, 146.7, 142.8, 141.0, 140.9, 138.2, 137.0, 134.9, 133.9, 128.7, 128.3, 127.4, 127.4, 127.2, 126.9, 126.5, 125.8, 125.3, 124.3, 124.0, 123.6, 115.3, 46.2, 45.1 ppm. MS (ESI): *m*/*z* (%) = 529 (30) $[M + 1 + Na]^+$, 528 (100) $[M + Na]^+$, 507 (16) $[M + 2]^+$, 506 (47) $[M + 1]^+$, 396 (38), 374 (24), 373 (41), 330 (21), 301 (25), 279 (61). $C_{29}H_{23}N_5O_4$ (505.52): calcd. C 68.90, H 4.59, N 13.85; found C 68.85, H 4.63, N 13.81.

5-Benzylbenzimidazo[2,1-*b*]quinazolin-12(5*H*)-ones 7: CuI (0.33 g, 1.71 mmol) was added under nitrogen to a solution of a 3-aryl-2-(benzylamino)-3*H*-quinazolin-4-one **5** (0.34 mmol) in anhydrous diglyme (20 mL). The mixture was stirred at room temperature for 30 min. NaH (0.075 g, 1.88 mmol) was then added, and the resulting mixture was stirred at 100 °C for 24 h. The solution was poured into aq. NH_4OH (5%, 200 mL) and stirred for 1 h, followed by extraction with CH_2Cl_2 (3 × 150 mL). The combined organic layers were washed with H_2O and dried ($MgSO_4$). After filtration, the solvent was removed under reduced pressure, and the residual material was chromatographed on a silica gel column with EtOAc/*n*-hexane (2:3) to give **7** in good yields.

5-Benzylbenzimidazo[2,1-*b*]quinazolin-12(5*H*)-one (7a): This compound (88 mg, 80%) was obtained as white prisms, m.p. 218–220 (CH_2Cl_2/*n*-hexane, 2:3). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.57 (dd, *J* = 7.6, 1.0 Hz, 1 H), 8.35 (dd, *J* = 8.0, 1.4 Hz, 1 H), 7.66 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1 H), 7.60 (dd, *J* = 8.3, 0.5 Hz, 1 H), 7.33–7.21 (m, 8 H), 7.09 (dd, *J* = 7.7, 0.6 Hz, 1 H), 5.42 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 160.0, 149.3, 146.7, 135.3, 134.4, 131.5, 128.9, 128.1, 127.5, 127.0, 126.0, 126.0, 125.8, 123.0, 122.2, 116.3, 116.3, 108.7, 45.6 ppm. MS (EI): *m*/*z* (%) = 326 (13) $[M + 1]^+$, 325 (57) $[M]^+$, 324 (16), 102 (12), 92 (21), 91 (100). $C_{21}H_{15}N_3O$ (325.36): calcd. C 77.52, H 4.65, N 12.91; found C 77.48, H 4.69, N 12.87.

5-Benzyl-8-bromobenzimidazo[2,1-*b*]quinazolin-12(5*H*)-one (7b): This compound (0.135 g, 75%) was obtained as white prisms, m.p. 261–263 (CH_2Cl_2/*n*-hexane, 2:3). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.41 (d, *J* = 8.5 Hz, 1 H), 8.33 (dd, *J* = 8.0, 1.6 Hz, 1 H), 7.67 (dd, *J* = 8.3, 1.6 Hz, 1 H), 7.59 (dd, *J* = 8.3, 0.7 Hz, 1 H), 7.34 (dd, *J* = 8.5, 1.8 Hz, 1 H), 7.31–7.24 (m, 6 H), 7.21 (d, *J* = 1.8 Hz, 1 H), 5.37 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 159.8, 149.1, 146.5, 134.8, 134.6, 132.8, 129.1, 128.3, 127.5, 127.0, 125.9, 125.2, 125.0, 123.4, 119.3, 117.3, 117.0, 111.8, 45.7 ppm. MS (EI): *m*/*z* (%) = 406 (7) $[M + 3]^+$, 405 (29) $[M + 2]^+$, 404 (11) $[M + 1]^+$, 403 (30) $[M]^+$, 205 (9), 204 (8), 102 (16), 91 (100). $C_{21}H_{14}BrN_3OBr$ (404.26): calcd. C 62.39, H 3.49, N 10.39; found C 62.33, H 3.53, N 10.33.

5-Benzyl-8-fluorobenzimidazo[2,1-*b*]quinazolin-12(5*H*)-one (7c): This compound (82 mg, 70%) was obtained as white prisms, m.p. 243–244 °C (CH_2Cl_2/*n*-hexane, 2:3). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.58 (dd, *J* = 8.8, 4.9 Hz, 1 H), 8.41 (ddd, *J* = 8.1, 1.5, 0.4 Hz, 1 H), 7.75 (ddd, *J* = 8.3, 6.9, 1.5 Hz, 1 H), 7.67 (dd, *J* = 8.3, 0.8 Hz, 1 H), 7.41–7.30 (m, 6 H), 6.99 (ddd, *J* = 9.4, 8.8, 2.4 Hz, 1 H), 6.86 (dd, *J* = 8.4, 2.4 Hz, 1 H), 5.46 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 161.0 (d, $^1J_{C,F}$ = 244.5 Hz), 159.7, 149.0, 147.0, 134.8, 134.5, 132.7 (d, $^3J_{C,F}$ = 12.5 Hz), 129.0, 128.3, 127.5, 126.9, 125.9, 123.3, 122.2 (d, $^4J_{C,F}$ = 2.1 Hz), 117.2 (d, $^3J_{C,F}$ = 9.7 Hz), 116.9, 109.0 (d, $^2J_{C,F}$ = 24.1 Hz), 96.9 (d, $^2J_{C,F}$ = 29.1 Hz), 45.8 ppm. MS (EI): *m*/*z* (%) = 345 (4) $[M + 2]^+$, 344 (31) $[M + 1]^+$, 343 (65) $[M]^+$, 342 (21), 252 (21), 224 (17), 102 (19), 91 (100). $C_{21}H_{14}FN_3O$ (343.35): calcd. C 73.46, H 4.11, N 12.24; found C 73.41, H 4.15, N 12.18.

5-Benzyl-9-nitrobenzimidazo[2,1-*b*]quinazolin-12(5*H*)-one (7d): This compound (92 mg, 73%) was obtained as white prisms, m.p. 280–282 °C (CH_2Cl_2/*n*-hexane, 2:3). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 9.16 (d, *J* = 2.4 Hz, 1 H), 8.40 (dd, *J* = 8.9, 2.4 Hz, 1 H), 8.30 (dd, *J* = 8.0, 1.5 Hz, 1 H), 7.84 (ddd, *J* = 8.3, 7.1, 1.5 Hz,

1 H), 7.67 (d, J = 8.9 Hz, 2 H), 7.47–7.42 (m, 3 H), 7.36–7.28 (m, 3 H), 5.60 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 159.1, 148.5, 147.3, 141.6, 136.8, 135.8, 135.0, 128.8, 127.9, 127.4, 126.6, 125.9, 125.5, 123.9, 122.6, 116.8, 110.3, 109.3, 45.0 ppm. MS (EI): m/z (%) = 371 (6) $[M + 1]^+$, 370 (24) $[M]^+$, 91 (100). $C_{21}H_{14}N_4O_3$ (370.36): calcd. C 68.10, H 3.81, N 15.13; found C 68.05, H 3.84, N 15.07.

Benzimidazo[2,1-*b*]quinazolin-12(5*H*)-ones 8: A solution of the appropriate 5-benzylbenzimidazo[2,1-*b*]quinazolin-12(5*H*)-one **7** (0.31 mmol) in triflic acid (5 mL) was stirred under nitrogen at 70 °C for 36 h. After the mixture had been cooled to 0 °C, MeOH (8 mL) was added, and the resulting mixture was stirred for 5 min. Afterwards, a solution of NH_4OH (30%) was added until pH = 7 was reached, and the solution was extracted with EtOAc (3 × 50 mL). The combined organic extracts were dried ($MgSO_4$), the solvent was removed under reduced pressure, and the residue was chromatographed on a silica gel column with CH_2Cl_2/MeOH (9:1) as eluent to give the compounds **8**.

Benzimidazo[2,1-*b*]quinazolin-12(5*H*)-one (8a): This compound (50 mg, 70%) was obtained as white prisms, m.p. >300 °C (CH_2Cl_2/*n*-hexane, 2:3). ^{1}H NMR (300 MHz, [D$_6$]DMSO, 70 °C): δ = 12.32 (br. s, 1 H), 8.42 (d, J = 7.8 Hz, 1 H), 8.24 (dd, J = 8.0, 1.2 Hz, 1 H), 7.76 (ddd, J = 8.3, 7.1, 1.2 Hz, 1 H), 7.52 (dd, J = 8.3, 1.1 Hz, 1 H), 7.47 (dd, J = 8.0, 1.5 Hz, 1 H), 7.42 (ddd, J = 8.0, 7.3, 1.2 Hz, 1 H), 7.32 (ddd, J = 8.0, 7.1, 1.1 Hz, 1 H), 7.28 (ddd, J = 7.8, 7.3, 1.5 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO, 70 °C): δ = 158.6, 146.7, 145.2, 135.6, 134.1, 126.8, 126.3, 125.3, 121.7, 121.1, 120.6, 114.5, 114.4, 112.6 ppm. MS (EI): m/z (%) = 235 (100) $[M]^+$, 207 (32), 205 (40), 179 (15), 104 (12), 103 (31), 90 (100). $C_{14}H_9N_3O$ (235.24): calcd. C 71.48, H 3.86, N 17.86; found C 71.43, H 3.93, N 17.81.

8-Bromobenzimidazo[2,1-*b*]quinazolin-12(5*H*)-one (8b): This compound (66 mg, 68%) was obtained as white prisms, m.p. >300 °C (CH_2Cl_2/*n*-hexane, 2:3). ^{1}H NMR (400 MHz, [D$_6$]DMSO, 70 °C): δ = 12.70 (br. s, 1 H), 8.28 (d, J = 8.4 Hz, 1 H), 8.21 (dd, J = 8.0, 1.3 Hz, 1 H), 7.78 (ddd, J = 8.3, 7.1, 1.3 Hz, 1 H), 7.65 (d, J = 1.8 Hz, 1 H), 7.50 (d, J = 8.3 Hz, 1 H), 7.40 (dd, J = 8.4, 1.8 Hz, 1 H), 7.33 (ddd, J = 8.0, 7.1, 0.9 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 70 °C): δ = 158.4, 147.4, 143.0, 140.3, 134.6, 126.9, 126.7, 123.2, 122.0, 119.2, 117.4, 116.8, 115.8, 113.8 ppm. MS (EI): m/z (%) = 315 (95) $[M + 1]^+$, 313 (100) $[M]^+$, 234 (24), 206 (25), 179 (11), 103 (18), 102 (19), 90 (12). $C_{14}H_8BrN_3O$ (314.14): calcd. C 53.53, H 2.57, N 13.38; found C 53.48, H 2.61, N 13.32.

8-Fluorobenzimidazo[2,1-*b*]quinazolin-12(5*H*)-one (8c): This compound (53 mg, 65%) was obtained as white prisms, m.p. >300 °C (CH_2Cl_2/*n*-hexane, 2:3). ^{1}H NMR (400 MHz, [D$_6$]DMSO, 70 °C): δ = 12.57 (br. s, 1 H), 8.35 (dd, J = 8.7, 5.1 Hz, 1 H), 8.22 (dd, J = 8.0, 1.2 Hz, 1 H), 7.78 (ddd, J = 8.2, 7.2, 1.2 Hz, 1 H), 7.51 (d, J = 8.2 Hz, 1 H), 7.33 (dd, J = 8.0, 7.2 Hz, 1 H), 7.29 (dd, J = 9.4, 2.4 Hz, 1 H), 7.07 (ddd, J = 9.8, 8.7, 2.4 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO, 70 °C): δ = 160.2 (d, $^1J_{C,F}$ = 239.1 Hz), 158.4, 147.8, 143.0, 139.6, 134.6, 126.7, 124.3, 122.1, 119.4, 115.3 (d, $^3J_{C,F}$ = 10.2 Hz), 113.8, 107.6 (d, $^2J_{C,F}$ = 24.8 Hz), 101.2 (d, $^2J_{C,F}$ = 27.2 Hz) ppm. MS (EI): m/z (%) = 254 (42) $[M + 1]^+$, 253 (100) $[M]^+$, 225 (52), 224 (46), 197 (12), 103 (18), 90 (7). $C_{14}H_8FN_3O$ (253.23): calcd. C 66.40, H 3.18, N 16.59; found C 66.35, H 3.23, N 16.52.

9-Nitrobenzimidazo[2,1-*b*]quinazolin-12(5*H*)-one (8d): This compound (57 mg, 66%) was obtained as white prisms, m.p. >300 °C (CH_2Cl_2/*n*-hexane, 2:3). ^{1}H NMR (400 MHz, [D$_6$]DMSO, 70 °C): δ = 12.49 (br. s, 1 H), 9.10 (d, J = 2.4 Hz, 1 H), 8.30 (dd, J = 8.9, 2.4 Hz, 1 H), 8.25 (dd, J = 8.0, 1.2 Hz, 1 H), 7.83 (ddd, J = 8.3, 7.3, 1.2 Hz, 1 H), 7.62 (d, J = 8.9 Hz, 1 H), 7.55 (d, J = 8.3 Hz, 1 H), 7.39 (ddd, J = 8.0, 7.3, 0.9 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 70 °C): δ = 158.2, 149.6, 145.4, 141.8, 140.5, 135.0, 127.4, 126.8, 122.7, 121.3, 118.7, 114.5, 113.7, 109.9 ppm. MS (EI): m/z (%) = 281 (17) $[M + 1]^+$, 280 (100) $[M]^+$, 250 (30), 248 (31), 235 (55), 234 (74), 207 (39), 130 (37), 103 (21), 90 (23). $C_{14}H_8N_4O_3$ (280.24): calcd. C 60.00, H 2.88, N 19.99; found C 59.94, H 2.95, N 19.93.

3-Aryl-2-mercapto-3*H*-quinazolin-4-ones 9: A solution of the appropriate iminophosphorane **4** (2.72 mmol) and carbon disulfide (6.6 mL) in anhydrous toluene (20 mL) was heated at 100 °C in a sealed tube for 12 h. The solvent was then removed under reduced pressure, and the residue was chromatographed on a silica gel column with EtOAc/*n*-hexane (3:2) as eluent to give the compounds **9** as a white solid.

3-(2-Bromophenyl)-2-mercapto-3*H*-quinazolin-4-one (9a): This compound (0.64 g, 70%) was obtained as white prisms, m.p. 262–264 °C (CH_2Cl_2/*n*-hexane, 2:3). ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 13.17 (s, 1 H), 7.97 (dd, J = 8.0, 1.2 Hz, 1 H), 7.81 (ddd, J = 8.0, 7.3, 1.5 Hz, 1 H), 7.75 (dd, J = 7.8, 1.1 Hz, 1 H), 7.53–7.45 (m, 3 H), 7.39–7.34 (m, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C): δ = 175.0, 159.0, 139.7, 138.1, 136.1, 132.8, 131.3, 130.3, 128.7, 127.5, 124.7, 122.4, 115.9, 115.7 ppm. MS (EI): m/z (%) = 353 (100) $[M – Br]^+$, 252 (27), 224 (17), 127 (16), 90 (14). $C_{14}H_9BrN_2OS$ (333.20): calcd. C 50.46, H 2.72, N 8.41; found C 50.41, H 2.77, N 8.36.

3-(2,4-Dibromophenyl)-2-mercapto-3*H*-quinazolin-4-one (9b): This compound (0.83 g, 74%) was obtained as white prisms, m.p. 261–262 °C (CH_2Cl_2/*n*-hexane, 2:3). ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 13.22 (s, 1 H), 8.03 (d, J = 2.1 Hz, 1 H), 7.98 (dd, J = 8.2, 1.2 Hz, 1 H), 7.81 (ddd, J = 8.2, 7.3, 1.5 Hz, 1 H), 7.73 (dd, J = 8.4, 2.1 Hz, 1 H), 7.48 (d, J = 8.4 Hz, 1 H), 7.46 (dd, J = 7.9, 1.5 Hz, 1 H), 7.37 (ddd, J = 7.9, 7.3, 1.2 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C): δ = 174.7, 158.9, 139.6, 137.7, 136.0, 134.8, 132.9, 131.7, 127.4, 124.6, 123.7, 122.1 (2 C), 115.9, 115.6 ppm. MS (EI): m/z (%) = 334 (33) $[M + 2 – Br]^+$, 332 (100) $[M + 1 – Br]^+$, 331 (39) $[M – Br]^+$, 330 (96), 223 (30), 133 (29), 102 (18), 90 (18). $C_{14}H_8Br_2N_2OS$ (412.10): calcd. C 40.80, H 1.96, N 6.80; found C 40.73, H 2.05, N 6.72.

3-(2-Bromo-4-fluorophenyl)-2-mercapto-3*H*-quinazolin-4-one (9c): This compound (0.60 g, 63%) was obtained as white prisms, m.p. 274–276 °C (CH_2Cl_2/*n*-hexane, 2:3). ^{1}H NMR (400 MHz, [D$_6$]-DMSO, 25 °C): δ = 13.20 (s, 1 H), 7.97 (d, J = 7.7 Hz, 1 H), 7.81 (dd, J = 7.7, 7.5 Hz, 1 H), 7.75 (dd, J = 8.4, 2.6 Hz, 1 H), 7.57 (dd, J = 8.8, 5.7 Hz, 1 H), 7.46 (d, J = 8.2 Hz, 1 H), 7.40 (ddd, J = 8.8, 8.5, 2.6 Hz, 1 H), 7.37 (dd, J = 8.2, 7.5 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C): δ = 175.1, 161.4 (d, $^1J_{C,F}$ = 249.2 Hz), 159.1, 139.7, 136.1, 134.8 (d, $^4J_{C,F}$ = 3.5 Hz), 132.6 (d, $^3J_{C,F}$ = 9.2 Hz), 127.5, 124.7, 123.2 (d, $^3J_{C,F}$ = 10.6 Hz), 120.0 (d, $^2J_{C,F}$ = 25.9 Hz), 115.9, 115.8 (d, $^2J_{C,F}$ = 21.4 Hz), 115.7 ppm. MS (EI): m/z (%) = 273 (23) $[M + 2 – Br]^+$, 272 (57) $[M + 1 – Br]^+$, 271 (100) $[M – Br]^+$, 270 (65), 243 (32), 242 (43), 136 (20), 108 (61), 92 (33), 90 (40). $C_{14}H_8BrFN_2OS$ (351.19): calcd. C 47.88, H 2.30, N 7.98; found C 47.84, H 2.37, N 7.92.

3-(2-Bromo-4-nitrophenyl)-2-mercapto-3*H*-quinazolin-4-one (9d): This compound (0.62 g, 60%) was obtained as white prisms, m.p. >300 °C (CH_2Cl_2/*n*-hexane, 2:3). ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 13.34 (s, 1 H), 8.56 (d, J = 2.7 Hz, 1 H), 8.22 (dd, J = 8.8, 2.7 Hz, 1 H), 8.09 (d, J = 8.8 Hz, 1 H), 7.99 (dd, J = 8.0, 1.1 Hz, 1 H), 7.86–7.81 (m, 1 H), 7.48 (d, J = 8.1 Hz, 1 H), 7.42 (m, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C): δ = 174.7,

159.1, 147.5, 139.7, 139.6, 136.2, 134.2, 130.9, 127.5, 126.6, 124.9, 124.8, 116.0, 115.8 ppm. MS (EI): *m*/*z* (%) = 379 (5) $[M + 2]^+$, 377 (10) $[M]^+$, 335 (12), 333 (10), 254 (33), 208 (22), 146 (30), 90 (100). $C_{14}H_8BrN_3O_3S$ (378.20): calcd. C 44.46, H 2.13, N 11.11; found C 44.41, H 2.19, N 11.03.

Benzo[4,5]thiazolo[2,3-*b*]quinazolin-12-ones 10: CuI (0.42 g, 2.2 mmol) was added under nitrogen to a solution of a 3-aryl-2-mercapto-3*H*-quinazolin-4-one **9** (0.44 mmol) in anhydrous diglyme (20 mL). The mixture was stirred at room temperature for 30 min. NaH (0.097 g, 2.42 mmol) was then added, and the resulting mixture was stirred at 150 °C for 12 h. The solution was poured into aq. NH_4OH (5%, 200 mL) and stirred for 1 h, followed by extraction with CH_2Cl_2 (3 × 100 mL). The combined organic layers were washed with H_2O and dried ($MgSO_4$). After filtration, the solvent was removed under reduced pressure, and the residual material was chromatographed on a silica gel column with EtOAc/*n*-hexane (2:3) to give the compounds **10** in good yield.

Benzo[4,5]thiazolo[2,3-*b*]quinazolin-12-one (10a): This compound (91 mg, 75%) was obtained as white prisms, m.p. 193–195 °C (EtOAc/*n*-hexane, 2:3). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.19 (dd, *J* = 8.0, 1.2 Hz, 1 H, 1 H), 7.80 (ddd, *J* = 8.0, 2.6, 1.2 Hz, 1 H), 7.68–7.64 (m, 1 H), 7.59–7.56 (m, 1 H), 7.53–7.49 (m, 2 H), 7.45–7.43 (m, 1 H), 7.39–7.35 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 160.9, 152.1, 147.6, 134.9, 134.6, 134.3, 132.2, 131.4, 129.0, 127.5, 127.1, 126.7, 124.4, 120.0 ppm. MS (EI): *m*/*z* (%) = 253 (17) $[M + 1]^+$, 252 (100) $[M]^+$, 224 (26), 112 (11), 90 (15). $C_{14}H_8N_2OS$ (252.29): calcd. C 66.65, H 3.20, N 11.10; found C 66.61, H 3.27, N 11.07.

8-Bromobenzo[4,5]thiazolo[2,3-*b*]quinazolin-12-one (10b): This compound (0.10 g, 72%) was obtained as white prisms, m.p. 272–273 °C (EtOAc/*n*-hexane, 2:3). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.85 (d, *J* = 8.9 Hz, 1 H), 8.37 (dd, *J* = 8.0, 0.9 Hz, 1 H), 7.79–7.73 (m, 1 H), 7.70 (d, *J* = 1.8 Hz, 1 H), 7.62 (d, *J* = 8.3 Hz, 1 H), 7.55 (dd, *J* = 8.9, 1.8 Hz, 1 H), 7.47–7.42 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 160.7, 156.2, 147.2, 135.1, 133.7, 130.0, 127.2, 126.2, 126.1, 125.8, 124.5, 120.4, 119.9, 118.6 ppm. MS (EI): *m*/*z* (%) = 332 (83) $[M + 2]^+$, 331 (39) $[M + 1]^+$, 330 (100) $[M]^+$, 304 (22), 223 (80), 133 (38), 90 (16). $C_{14}H_7BrN_2OS$ (331.19): calcd. C 50.77, H 2.13, N 8.46; found C 50.72, H 2.18, N 8.40.

8-Fluorobenzo[4,5]thiazolo[2,3-*b*]quinazolin-12-one (10c): This compound (96 mg, 80%) was obtained as white prisms, m.p. 217–219 °C (EtOAc/*n*-hexane, 2:3). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.98 (dd, *J* = 9.2, 4.8 Hz, 1 H), 8.30 (ddd, *J* = 8.1, 1.5, 0.5 Hz, 1 H), 7.76 (ddd, *J* = 8.3, 7.1, 1.5 Hz, 1 H), 7.64–7.61 (m, 1 H), 7.46 (ddd, *J* = 8.1, 7.1, 1.2 Hz, 1 H), 7.30 (dd, *J* = 7.6, 2.7 Hz, 1 H), 7.2 (ddd, *J* = 9.2, 8.6, 2.7 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 160.7 (d, $^1J_{C,F}$ = 248.7 Hz), 160.6, 156.5, 147.1, 135.0, 132.4 (d, $^3J_{C,F}$ = 1.5 Hz), 127.1, 126.1, 126.0, 125.5 (d, $^4J_{C,F}$ = 10.0 Hz), 120.6 (d, $^3J_{C,F}$ = 8.5 Hz), 118.6, 114.1 (d, $^2J_{C,F}$ = 23.1 Hz), 109.1 (d, $^2J_{C,F}$ = 27.4 Hz) ppm. MS (EI): *m*/*z* (%) = 272 (18) $[M + 2]^+$, 271 (43) $[M + 1]^+$, 270 (100) $[M]^+$, 242 (53), 241 (38), 121 (22), 108 (59), 90 (17). $C_{14}H_7FN_2OS$ (270.28): calcd. C 62.21, H 2.61, N 10.36; found C 62.17, H 2.66, N 10.29.

5,7-Dihydroquinazolino[3,2-*a*]quinazolin-12-one (11): A mixture of 2-[2-(benzylamino)-4-oxo-4*H*-quinazolin-3-yl]benzonitrile (**5e**, 0.2 g, 0.568 mmol), palladium on charcoal (10%, 0.2 g, 0.187 mmol) and formic acid (85%, 4 mL) in MeOH (20 mL) was warmed at 50 °C under nitrogen for 15 h. After cooling, the mixture was filtered through Celite, the solvent was removed under reduced pressure, and the resulting solid was recrystallized from EtOAc/*n*-hexane (1:1) to give compound **11** as white prisms (0.115 g, 80% yield), m.p. 189.9–192.1 °C. ^{1}H NMR (600 MHz, $[D_6]$DMSO, 25 °C): δ = 8.15 (d, *J* = 8.2 Hz, 1 H), 8.27 (d, *J* = 8.0 Hz, 1 H), 7.93 (br. s, 1 H), 7.61 (ddd, *J* = 8.1, 7.1, 1.6 Hz, 1 H), 7.36–7.33 (m, 2 H), 7.29–7.26 (m, 1 H), 7.21 (d, *J* = 8.1 Hz, 1 H), 7.16 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1 H), 4.29 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $[D_6]$DMSO, 25 °C): δ = 161.4, 151.7, 149.0, 135.1, 133.2, 128.4, 127.5, 127.4, 126.5, 126.9, 124.2, 122.5, 122.0, 118.3, 41.6 ppm. MS (EI): *m*/*z* (%) = 249 (30) $[M]^+$, 248 (43), 167 (34), 149 (100), 113 (13), 83 (13), 71 (30). $C_{15}H_{11}N_3O$ (249.27): calcd. C 72.28, H 4.45, N 16.86; found C 72.22, H 4.51, N 16.82.

6-Benzyl-5-imino-5,6-dihydroquinazolino[3,2-*a*]quinazolin-12-one (12): $NaBH_4$ (0.026 g, 0.682 mmol) in anhydrous THF (5 mL) was added at room temperature under nitrogen to a solution of 2-[2-(benzylamino)-4-oxo-4*H*-quinazolin-3-yl]benzonitrile (**5e**, 0.2 g, 0.568 mmol) in anhydrous THF (15 mL). The mixture was stirred at room temperature for 24 h. Afterwards, it was poured into cool H_2O (100 mL) and extracted with EtOAc (3 × 30 mL). The combined organic layers were dried ($MgSO_4$) and filtered, and the solvent was removed under reduced pressure. The resulting solid was recrystallized from EtOAc/*n*-hexane (1:1) to give compound **12** as white prisms (0.18 g, 90% yield), m.p. 167–169 °C. ^{1}H NMR (600 MHz, $[D_6]$DMSO, 25 °C): δ = 9.58 (s, 1 H), 8.70 (d, *J* = 8.5 Hz, 1 H), 8.27 (dd, *J* = 8.0, 1.0 Hz, 1 H), 8.09 (dd, *J* = 7.8, 0.9 Hz, 1 H), 7.71 (ddd, *J* = 8.1, 7.3, 0.9 Hz, 1 H), 7.67 (ddd, *J* = 8.5, 7.4, 1.0 Hz, 1 H), 7.51 (dd, *J* = 7.9, 7.4 Hz, 1 H), 7.43 (d, *J* = 7.5 Hz, 5 H), 7.40 (d, *J* = 8.1 Hz, 1 H), 7.33 (dd, *J* = 7.8, 7.3 Hz, 1 H), 7.25 (dd, *J* = 7.7, 7.5 Hz, 1 H), 7.17 (dd, *J* = 7.7, 7.3 Hz, 1 H), 5.70 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $[D_6]$DMSO, 25 °C): δ = 161.5, 153.0, 146.3, 144.1, 138.0, 135.1, 132.2, 131.5, 128.0, 127.5, 127.1, 126.7, 126.6, 126.2, 125.2, 124.2, 121.5, 118.9, 118.2, 46.1 ppm. MS (ESI): *m*/*z* (%) = 375 (21) $[M + Na]^+$, 355 (20), $[M + 2]^+$, 354 (100) $[M + 1]^+$. $C_{22}H_{16}N_4O$ (352.39): calcd. C 74.98, H 4.58, N 15.90; found C 74.93, H 4.63, N 15.82.

5-Aminoquinazolino[3,2-*a*]quinazolin-12-one (13): A solution of 6-benzyl-5-imino-5,6-dihydroquinazolino[3,2-*a*]quinazolin-12-one (**12**, 0.1 g, 0.29 mmol) in dry EtOH (20 mL) in the presence of palladium on charcoal (10%, 0.062 g, 0.058 mmol) was stirred under hydrogen at room temperature for 48 h. The mixture was filtered through Celite, the solvent was removed at reduced pressure, and the resulting solid was recrystallized from EtOAc/*n*-hexane (1:1) to give compound **13** as white prisms (0.05 g, 67% yield), m.p. >300 °C. ^{1}H NMR (300 MHz, $[D_6]$DMSO, 25 °C): δ = 9.26 (d, *J* = 8.8 Hz, 1 H), 8.49 (br. s, 1 H), 8.36 (br. s, 1 H), 8.28 (dd, *J* = 8.0, 1.3 Hz, 1 H), 8.13 (dd, *J* = 8.8, 1.4 Hz, 1 H), 7.81 (ddd, *J* = 8.8, 7.3, 1.3 Hz, 1 H), 7.73 (ddd, *J* = 8.2, 7.6, 1.4 Hz, 1 H), 7.58 (dd, *J* = 8.0, 7.3 Hz, 1 H), 7.46 (d, *J* = 8.2 Hz, 1 H), 7.31 (dd, *J* = 8.0, 7.6 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $[D_6]$DMSO, 25 °C): δ = 162.8, 159.2, 148.1, 147.9, 137.3, 134.8, 132.9, 127.0, 126.4, 124.9, 124.4, 123.4, 120.9, 117.7, 114.0 ppm. MS (EI): *m*/*z* (%) = 262 (100) $[M]^+$, 236 (29), 233 (26), 220 (17), 145 (24), 144 (22), 120 (34), 119 (30), 117 (36), 102 (39), 90 (41). $C_{15}H_{10}N_4O$ (262.27): calcd. C 68.69, H 3.84, N 21.36; found C 68.62, H 3.89, N 21.30.

6-Benzyl-5-imino-6,12-dihydro-5*H*-quinazolino[3,2-*a*]quinazolin-12-ol (14): A solution of 2-[2-(benzylamino)-4-oxo-4*H*-quinazolin-3-yl]benzonitrile (**5e**, 0.27 g, 0.77 mmol) in anhydrous THF (30 mL) was cooled to 0 °C, and $LiAlH_4$ (1 M solution in THF, 0.8 mL, 0.8 mmol) was added slowly under nitrogen. The reaction mixture was warmed at room temperature and stirred for 2 h. Afterwards, it was poured into H_2O (100 mL) and extracted with EtOAc (3 × 40 mL). The combined organic layers were dried ($MgSO_4$) and filtered, and the solvent was removed under reduced pressure. The residual solid was recrystallized from EtOAc/*n*-hexane (1:1) to give compound **14** as white prisms (0.19 g, 70% yield), m.p. 178–180 °C.

^{1}H NMR (600 MHz, [D$_6$]DMSO, 25 °C): δ = 8.98 (s, 1 H), 8.19 (d, J = 7.8 Hz, 1 H), 7.77 (d, J = 8.6 Hz, 1 H), 7.65–7.62 (m, 1 H), 7.42 (d, J = 7.6 Hz, 2 H), 7.37 (d, J = 7.3 Hz, 1 H), 7.28–7.24 (m, 4 H), 7.16 (t, J = 7.2 Hz, 1 H), 7.06 (t, J = 7.3 Hz, 1 H), 7.03 (dd, J = 7.9, 0.9 Hz, 1 H), 7.01 (d, J = 8.9 Hz, 1 H), 6.85 (d, J = 8.9 Hz, 1 H), 5.74 (d, J = 14.4 Hz, 1 H), 5.64 (d, J = 14.4 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C): δ = 153.5, 142.4, 140.9, 138.8, 136.3, 132.7, 129.2, 127.9, 127.6, 127.2, 126.3, 123.1, 123.0, 122.7, 122.6, 115.6, 115.2, 74.7, 45.1 ppm. MS (ESI): m/z (%) = 356 (17) [M + 2]$^+$, 355 (100) [M + 1]$^+$, 338 (14), 337 (56), 327 (20), 247 (21). $C_{22}H_{18}N_4O$ (354.40): calcd. C 74.56, H 5.12, N 15.81; found C 74.51, H 5.20, N 15.73.

3-(2-Aminophenyl)-2-(benzylamino)-3*H*-quinazolin-4-one (15): A solution of 2-(benzylamino)-3-(2-nitrophenyl)-3*H*-quinazolin-4-one (**5f**, 0.1 g, 0.27 mmol) in anhydrous THF (30 mL) in the presence of palladium on charcoal (10%, 0.086 g, 0.08 mmol) was stirred under hydrogen at room temperature for 2 h. The mixture was filtered through Celite, the solvent was removed under reduced pressure, and the resulting solid was recrystallized from CH_2Cl_2/*n*-hexane (1:1) to give the diamino compound **15** as white prisms (0.073 g, 80% yield), m.p. 166–168 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.15 (ddd, J = 7.9, 1.6, 0.4 Hz, 1 H), 7.63 (ddd, J = 8.3, 7.1, 1.6 Hz, 1 H), 7.44 (dd, J = 8.3, 1.1 Hz, 1 H), 7.32–7.22 (m, 6 H), 7.19 (ddd, J = 7.9, 7.1, 1.1 Hz, 1 H), 7.10 (dd, J = 8.2, 1.5 Hz, 1 H), 6.92–6.88 (m, 2 H), 4.73–4.71 (m, 1 H), 4.68 (dd, J = 6.1, 2.2 Hz, 2 H), 3.74 (br. s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 162.1, 149.6, 149.3, 143.6, 138.4, 134.8, 131.1, 129.3, 128.6, 127.7, 127.2, 125.0, 127.7, 120.0, 119.6, 117.6, 117.5, 45.3 ppm. MS (EI): m/z (%) = 343 (7) [M + 1]$^+$, 342 (24) [M]$^+$, 324 (22), 322 (23), 236 (25), 234 (73), 219 (70), 182 (100), 180 (75), 106 (35), 90 (35). $C_{21}H_{18}N_4O$ (342.39): calcd. C 73.67, H 5.30, N 16.36; found C 73.61, H 5.38, N 16.29.

6-Aminobenzo[4,5]imidazo[1,2-*c*]quinazoline (16): Phosphorus pentachloride (0.06 g, 0.29 mmol) was added under nitrogen at 0 °C to a solution of 3-(2-aminophenyl)-2-(benzylamino)-3*H*-quinazolin-4-one (**15**, 0.1 g, 0.29 mmol) in dry toluene (20 mL). The reaction mixture was stirred at room temperature for 1 h. Triethylamine (0.029 g, 0.29 mmol) was added, and the resulting mixture was heated at reflux temperature and stirred for 1 h. The mixture was poured into ice/H_2O (200 mL) and extracted with EtOAc (3 × 100 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated to dryness. The resulting solid was recrystallized from EtOAc/*n*-hexane (1:1) to give compound **16** (0.053 g, 78% yield) as white prisms, m.p. >300 °C (EtOAc/*n*-hexane, 1:1). ^{1}H NMR (400 MHz, [D$_7$]DMF, 80 °C): δ = 8.49 (d, J = 7.9 Hz, 1 H), 8.30 (dd, J = 8.0, 1.6 Hz, 1 H), 7.77 (ddd, J = 8.3, 7.1, 1.6 Hz, 1 H), 7.58 (d, J = 8.3 Hz, 1 H), 7.51 (d, J = 7.9 Hz, 1 H), 7.46–7.42 (m, 1 H), 7.36–7.28 (m, 2 H), 3.08 (br. s, 2 H) ppm. ^{13}C NMR (100 MHz, [D$_7$]DMF, 80 °C): δ = 159.3, 147.5, 146.3, 136.1, 134.4, 127.7, 126.8, 125.7, 122.1, 121.9, 121.1, 115.3, 115.1, 112.8 ppm. MS (EI): m/z (%) = 235 (100) [M + 1]$^+$, 207 (33), 206 (37), 179 (15), 117 (18), 103 (52), 91 (31). $C_{14}H_{10}N_4$ (234.26): calcd. C 71.78, H 4.30, N 23.92; found C 71.73, H 4.39, N 23.87.

1-Substituted 3-[2-(4-Methylene-4*H*-benzo[*d*][1,3]oxazin-2-yl)phenyl]ureas 19: The appropriate isocyanate (1.56 mmol) was added at room temperature under nitrogen to a solution of *N*-(2-acetylphenyl)-2-(triphenylphosphoranylideneamino)benzamide (**4g**, 0.4 g, 0.78 mmol) in dry toluene (40 mL). The resulting mixture was warmed at reflux temperature for 6–12 h. After removal of the solvent under reduced pressure, the residue was recrystallized from EtOAc/*n*-hexane (1:1).

1-Ethyl-3-[2-(4-methylene-4*H*-benzo[*d*][1,3]oxazin-2-yl)phenyl]urea (19a): This compound (0.20 g, 85%) was obtained as white prisms, m.p. 191–193 °C (EtOAc/*n*-hexane, 1:1). ^{1}H NMR (400 MHz, [D$_6$]-DMSO, 25 °C): δ = 11.06 (s, 1 H), 8.39 (d, J = 8.8 Hz, 1 H), 8.0 (d, J = 8.2 Hz, 1 H), 7.72 (d, J = 7.9 Hz, 1 H), 7.63 (d, J = 8.0 Hz, 1 H), 7.49–7.43 (m, 2 H), 7.32 (dd, J = 7.9, 7.4 Hz, 1 H), 7.17 (br. s, 1 H), 7.02 (dd, J = 8.2, 7.4 Hz, 1 H), 5.14 (d, J = 2.9 Hz, 1 H), 4.82 (d, J = 2.9 Hz, 1 H), 3.18 (q, J = 7.2 Hz, 2 H), 1.11 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 154.8, 154.5, 150.3, 141.9, 136.8, 132.4, 130.9, 128.4, 128.1, 126.2, 123.0, 120.0, 119.7, 119.4, 113.9, 87.2, 34.2, 15.1 ppm. MS (EI): m/z (%) = 307 (25) [M]$^+$, 263 (99), 235 (100), 219 (43), 146 (26). $C_{18}H_{17}N_3O_2$ (307.35): calcd. C 70.34, H 5.58, N 13.67; found C 70.27, H 5.63, N 13.62.

1-[2-(4-Methylene-4*H*-benzo[*d*][1,3]oxazin-2-yl)phenyl]-3-propylurea (19b): This compound (0.195 g, 78%) was obtained as white prisms, m.p. 194–195 °C (EtOAc/*n*-hexane, 1:1). ^{1}H NMR (400 MHz, [D$_6$]-DMSO, 25 °C): δ = 11.04 (s, 1 H), 8.37 (dd, J = 8.5, 0.9 Hz, 1 H), 8.0 (dd, J = 8.1, 1.6 Hz, 1 H), 7.70 (dd, J = 8.0, 1.2 Hz, 1 H), 7.62 (dd, J = 7.7, 0.7 Hz, 1 H), 7.48–7.42 (m, 2 H), 7.31 (ddd, J = 8.0, 7.4, 0.7 Hz, 1 H), 7.15 (t, J = 5.2 Hz, 1 H), 7.01 (ddd, J = 8.1, 7.2, 0.9 Hz, 1 H), 5.12 (d, J = 2.8 Hz, 1 H), 4.81 (d, J = 2.8 Hz, 1 H), 3.10 (q, J = 6.5 Hz, 2 H), 1.51 (m, 2 H), 0.90 (t, J = 7.3 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 154.7, 154.6, 150.3, 141.9, 136.8, 132.3, 130.8, 128.3, 128.0, 126.2, 122.9, 119.9, 119.7, 119.5, 114.0, 87.1, 41.2, 22.6, 11.1 ppm. MS (EI): m/z (%) = 321 (19) [M]$^+$, 264 (60), 263 (78), 236 (31), 235 (100), 219 (39), 146 (26), 118 (28). $C_{19}H_{19}N_3O_2$ (321.37): calcd. C 71.01, H 5.96, N 13.08; found C 70.96, H 6.02, N 13.02.

1-[2-(4-Methylene-4*H*-benzo[*d*][1,3]oxazin-2-yl)phenyl]-3-phenylurea (19c): This compound (0.224 g, 80%) was obtained as white prisms, m.p. 240–242 °C (EtOAc/*n*-hexane, 1:1). ^{1}H NMR (300 MHz, [D$_6$]-DMSO, 25 °C): δ = 11.36 (s, 1 H), 9.69 (s, 1 H), 8.27 (dd, J = 8.5, 0.9 Hz, 1 H), 8.05 (dd, J = 8.1, 1.6 Hz, 1 H), 7.73 (dd, J = 7.8, 1.2 Hz, 1 H), 7.59–7.49 (m, 4 H), 7.46 (dt, J = 7.6, 1.2 Hz, 1 H), 7.34–7.26 (m, 3 H), 7.11 (ddd, J = 8.1, 7.6, 0.9 Hz, 1 H), 7.00 (dt, J = 7.4, 1.0 Hz, 1 H), 5.16 (d, J = 2.8 Hz, 1 H), 4.83 (d, J = 2.8 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C): δ = 154.7, 152.4, 150.4, 141.0, 139.6, 136.8, 132.5, 131.0, 128.7, 128.6, 128.3, 126.5, 123.1, 122.3, 121.1, 120.5, 119.8, 119.2, 115.1, 87.5 ppm. MS (EI): m/z (%) = 356 (26) [M + 1]$^+$, 355 (76) [M]$^+$, 262 (98), 235 (99), 219 (61), 217 (46), 206 (37), 205 (35), 146 (55), 119 (34), 116 (35), 90 (100). $C_{22}H_{17}N_3O_2$ (355.39): calcd. C 74.35, H 4.82, N 11.82; found C 74.30, H 4.87, N 11.76.

1-(4-Methoxyphenyl)-3-[2-(4-methylene-4*H*-benzo[*d*][1,3]oxazin-2-yl)phenyl]urea (19d): This compound (0.224 g, 75%) was obtained as white prisms, m.p. 223–226 °C (EtOAc/*n*-hexane, 1:1). ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 11.32 (s, 1 H), 9.46 (s, 1 H), 8.28 (d, J = 7.8 Hz, 1 H), 8.05 (dd, J = 8.1, 1.5 Hz, 1 H), 7.73 (d, J = 7.7 Hz, 1 H), 7.53–7.48 (m, 1 H), 7.44 (d, J = 8.03 Hz, 1 H), 7.40 (d, J = 8.4 Hz, 2 H), 7.33–7.29 (m, 1 H), 7.11–7.07 (m, 1 H), 6.89 (d, J = 8.4 Hz, 2 H), 6.87–6.83 (m, 1 H), 5.16 (d, J = 2.8 Hz, 1 H), 4.83 (d, J = 2.8 Hz, 1 H), 3.71 (s, 3 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 155.0, 154.7, 152.5, 150.3, 141.2, 136.8, 132.4, 130.9, 130.3, 128.4, 128.1, 126.3, 123.0, 121.3, 120.7, 120.2, 119.8, 114.9, 113.7, 87.5, 55.1 ppm. MS (EI): m/z (%) = 385 (9) [M]$^+$, 384 (13), 263 (64), 235 (100), 219 (36), 149 (30), 146 (44), 123 (71),108 (32). $C_{23}H_{19}N_3O_3$ (385.14): calcd. C 71.67, H 4.97, N 10.90; found C 71.61, H 5.05, N 10.83.

1-Benzyl-3-[2-(4-methylene-4*H*-benzo[*d*][1,3]oxazin-2-yl)phenyl]urea (19e): This compound (0.244 g, 85%) was obtained as white prisms, m.p. 169–172 °C (EtOAc/*n*-hexane, 1:1). ^{1}H NMR (600 MHz, [D$_6$]-DMSO, 25 °C): δ = 11.21 (s, 1 H), 8.41 (dd, J = 8.5, 1.2 Hz, 1 H), 8.03 (dd, J = 8.1, 1.7 Hz, 1 H), 7.77 (t, J = 6.0 Hz, 1 H), 7.72 (dd,

Table 9. Crystal data for **6d**, **14** and **19e**.

	6d	**14**	**19e**
Empirical formula	$C_{29}H_{22}BrN_5O_4$	$C_{22}H_{18}N_4O$	$C_{23}H_{19}N_3O_2$
Crystal size [mm]	$0.25 \times 0.09 \times 0.06$	$0.26 \times 0.05 \times 0.04$	$0.40 \times 0.15 \times 0.09$
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	*Pbca*	*P*2(1)/*c*	*P*2(1)/*c*
a [Å]	16.5034(6)	10.2462(7)	4.7354(2)
b [Å]	8.8217(3)	22.6820(14)	38.794(2)
c [Å]	35.1457(12)	10.9986(7)	9.9132(5)
α [°]	90	90	90
β [°]	90	101.928(2)	98.697(2)
γ [°]	90	90	90
V [Å^3]	5116.8(3)	1721.57(18)	1592.92(12)
Z	8	4	4
λ [Å]	0.71073	0.71073	0.71073
$\rho_{calcd.}$ [Mg m^{-3}]	1.517	1.367	1.363
F(000)	2384	744	776
T [K]	100(2)	100(2)	100(2)
μ [mm^{-1}]	1.653	0.087	0.089
θ range [°]	1.69–28.26	2.09–28.20	2.10–26.37
Index ranges	$-21 \le h \le 21$	$-9 \le h \le 9$	$-5 \le h \le 14$
	$-11 \le k \le 11$	$-29 \le h \le 30$	$-48 \le k \le 48$
	$-46 \le l \le 44$	$-14 \le h \le 14$	$-12 \le l \le 12$
Reflections collected	55934	19698	19681
Independent reflections	6114	4012	3669
R_{int}	0.0567	0.044	0.049
Refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2
Data/restraints/parameters	6114/0/356	4012/9/252	3669/0/298
GOOF on F^2	1.033	1.149	1.038
R_1[a]	0.035	0.068	0.039
wR_2[b]	0.084	0.146	0.097
Largest difference peak [e Å^{-3}]	0.413/–0.351	0.435/–0.279	0.215/–0.181

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for reflections with $I > 2\sigma(I)$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_o^2)/3$ and *a* and *b* are constants set by the program.

J = 8.0, 1.3 Hz, 1 H), 7.66 (d, *J* = 7.8 Hz, 1 H), 7.49–7.44 (m, 2 H), 7.37–7.30 (m, 5 H), 7.25–7.23 (m, 1 H), 7.06 (ddd, *J* = 8.1, 7.2, 1.3 Hz, 1 H), 5.14 (d, *J* = 2.9 Hz, 1 H), 4.83 (d, *J* = 2.9 Hz, 1 H), 4.38 (d, *J* = 6.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 154.7, 154.7, 150.3, 141.7, 140.2, 136.8, 132.3, 130.8, 128.3, 128.0, 128.0, 126.9, 126.4, 126.3, 122.9, 120.2, 119.7, 119.5, 114.1, 87.2, 42.8 ppm. MS (ESI): *m*/*z* (%) = 393 (16) [M + Na + 1]$^+$, 369 (100) [M]$^+$, 354 (45), 353 (96), 339 (21), 279 (59), 278 (41), 277 (86), 150 (51). $C_{23}H_{19}N_3O_2$ (369.42): calcd. C 74.78, H 5.18, N 11.37; found C 74.72, H 5.23, N 11.30.

1-(4-Methoxybenzyl)-3-[2-(4-methylene-4*H*-benzo[*d*][1,3]oxazin-2-yl)phenyl]urea (19f): This compound (0.273 g, 88%) was obtained as white prisms, m.p. 173–176 °C (EtOAc/*n*-hexane, 1:1). ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 11.23 (s, 1 H), 8.39 (dd, *J* = 8.5, 0.9 Hz, 1 H), 8.01 (dd, *J* = 8.1, 1.5 Hz, 1 H), 7.82 (t, *J* = 5.9 Hz, 1 H), 7.73 (dd, *J* = 7.9, 1.1 Hz, 1 H), 7.67 (d, *J* = 7.9 Hz, 1 H), 7.49–7.43 (m, 2 H), 7.31 (dt, *J* = 7.9, 1.2 Hz, 1 H), 7.25 (d, *J* = 8.7 Hz, 2 H), 7.03 (ddd, *J* = 8.1, 7.3, 0.9 Hz, 1 H), 6.88 (d, *J* = 8.7 Hz, 2 H) 5.16 (d, *J* = 2.8 Hz, 1 H), 4.82 (d, *J* = 2.8 Hz, 1 H), 4.27 (d, *J* = 5.9 Hz, 2 H), 3.71 (s, 3 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25 °C): δ = 158.1, 154.8, 154.7, 150.4, 141.9, 136.9, 132.6, 132.3, 131.0, 128.5, 128.4, 128.2, 126.5, 123.1, 120.3, 119.8, 119.6, 114.1, 113.7, 87.4, 55.0, 42.3 ppm. MS (EI): *m*/*z* (%) = 399 (75) [M]$^+$, 264 (39), 235 (23), 136 (49), 121 (100), 91 (17). $C_{24}H_{21}N_3O_3$ (399.00): calcd. C 72.16, H 5.30, N 10.52; found C 71.97, H 5.01, N 10.58.

Crystal Structure Determination: X-ray structure determinations of compounds **6d**, **14** and **19e** were carried out with a Bruker Smart APEX machine. Data were collected by use of monochromated Mo-K_α radiation in ω-scan mode (Table 9). The structures were solved by direct methods. All were refined anisotropically on F^2. The methyl groups were refined by use of rigid groups, and the other hydrogen atoms were refined with use of a riding model. Special features: For compound **6d**: the NH hydrogen atoms were refined freely; for compound **14**: the NH and OH hydrogen atoms were refined freely; for compound **19e**: the phenyl group C21–C26 is disordered over two positions. CCDC-716954 (**6d**), -716955 (**14**) and -716956 (**19e**) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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