Tetrahedron 70 (2014) 23–29

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Palladium-catalyzed carbonylative synthesis of *N*-(2-cyanoaryl) benzamides and sequential synthesis of quinazolinones

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ARTICLE INFO

Article history:
Received 1 November 2013
Received in revised form 13 November 2013
Accepted 18 November 2013
Available online 22 November 2013

Keywords:
Palladium catalyst
Carbonylation
$Mo(CO)_6$
Amide
Quinazolinone

ABSTRACT

A convenient procedure for the synthesis of *N*-(2-cyanoaryl)benzamides has been developed. Using aryl bromides and 2-aminobenzonitriles as the substrates, $Mo(CO)_6$ as the CO source, the desired amides were produced in good yields. Quinazolinones were produced in good yields in a sequential manner as well.

1. Introduction

Functionalized benzamides are an important class of compounds with broad applications in pharmaceuticals and advanced materials (Fig. 1).[1] Since the pioneering work of Schoenberg and Heck in 1974 on palladium-catalyzed aminocarbonylation of aryl halides,[2] impressive progresses have been realized in this area.[3] As expensive high-pressure equipment is needed to perform the reactions with this odorless, toxic, and flammable gas, synthetic chemists are usually reluctant to use CO gas-based carbonylation methodologies in laboratories.

Based on the interesting applications of carbonylation reactions and the above-mentioned limitations, many research groups are working on alternative CO sources exploration.[4] Such as, Larhed et al. did a great work on the carbonylative coupling chemistry with $Mo(CO)_6$ as CO precursor.[5] Amongst others, they reported the aminocarbonylation of aryl halides with $Mo(CO)_6$ under microwave irradiation.[6] So far, $Mo(CO)_6$ as CO source has also been applied for many other carbonylative coupling reactions, such as Suzuki-,[7] Stille-,[8] and Sonogashira-coupling.[9] Recently, Skrydstrup et al.

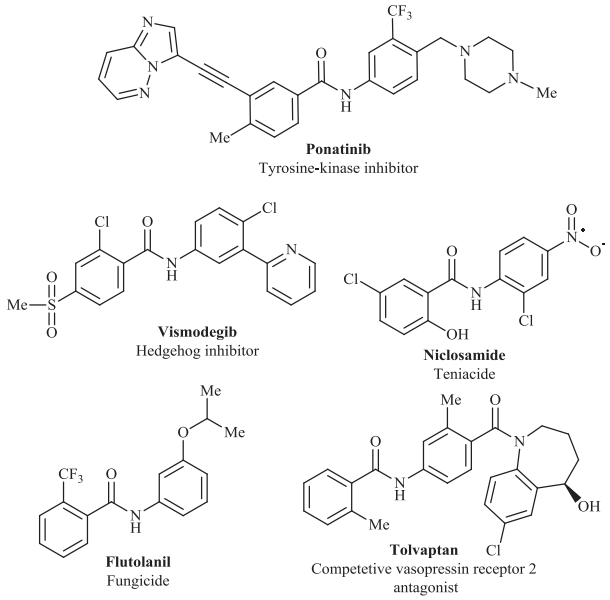

Fig. 1. Selected examples of biologically active benzamides.

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http://dx.doi.org/10.1016/j.tet.2013.11.055

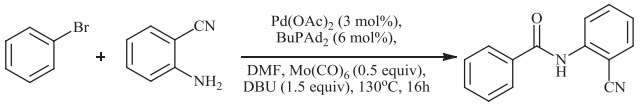
published a two-chamber carbonylation method via ex situ generation of CO from acid chloride derivatives.[10] Among the amides, benzanilides are an interesting analogue of compounds and many procedures have been reported for their preparation.[11] For example, the condensation of aniline with benzoic acid, oxidation procedures, and coupling reactions.

Palladium-catalyzed aminocarbonylation was applied in their preparation as well.[12] Such as the procedure developed by Beller et al. based on one-pot diazotization/aminocarbonylation of anilines to give symmetric benzamides using CO gas (10 bar) at 50 °C.[12a] More recently, Iranpoor et al. reported a $Mo(CO)_6$/norbornadiene-mediated aminocarbonylation of aryl iodides with electron-rich amines in diglyme.[13] However, to the best of our knowledge, the use of steric hindered and low nucleophilic anilines as nucleophiles are not reported.

2. Results

In this work we wish to present here a convenient palladium-catalyzed method to synthesize *N*-(2-cyanoaryl)benzamides from steric hindered 2-aminobenzonitriles. A range of the desired products has been isolated in good yields. Interestingly, $Mo(CO)_6$ was applied as a CO source in this procedure. CataCXium A® was proved to be the best ligand for this reaction. Additionally, the one-pot synthesis of quinazolinones from *N*-(2-cyanoaryl)benzamides was realized as well.

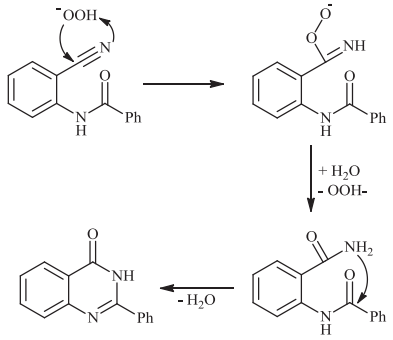
The general procedure for the synthesis of benzamides from aryl bromides and 2-aminobenzonitrile derivative has been shown in Scheme 1. The model reaction was performed with 2-aminobenzonitrile and 1.2 equiv of bromobenzene in DMF with 0.5 equiv $Mo(CO)_6$, under the assistant of $Pd(OAc)_2$ (3 mol %) and CataCXium A (6 mol %) at 130 °C for 16 h. DBU (1.5 equiv) was used as the base, which additionally acts as a promoter to assist the release of CO from $Mo(CO)_6$. In the absence of palladium catalyst, no desired amide could be observed. Temperatures below 130 °C lead to a drastically decrease of the conversion.



Scheme 1. Synthesis of *N*-(2-cyanoaryl)benzamides.

Furthermore, we investigated the urea hydroperoxide (UHP) mediated-cyclization of the obtained *N*-(2-cyanoaryl)benzamides to yield the corresponding quinazolinones. This structure holds very important applications in the pharmaceutical chemistry.[14] We performed the reactions directly in the vessel without further purification of the amides. The proposed mechanism for this transformation is shown in Scheme 2. The hydroperoxide anion attacks the nitrile group, followed by a rearrangement to give the quinazolinones after intramolecular condensation.[15]

The substrate-scope for the aminocarbonylation to yield amides is shown in Table 1. Various substituents and heteroaromatic 2-aminonitriles were tested and gave the desired products in moderate to good yields under standard conditions (Table 1, entries a1–12). But low conversion was observed when we try to apply 4-chloro-2-benzonitrile as substrate (Table 1, entry a2). Subsequently, different aryl bromides were tested with 2-aminobenzonitrile (Table 1, entries a13–25). In general, better results were obtained with electron withdrawing substituents (Table 1, entries a13, a14, a20), while heteroaromatic arenes gave lower yields (Table 1, entries a11, a12, a16, a23). The low stability of the Pd-arene



Scheme 2. Quinazolinones from *N*-(2-cyanoaryl)-benzamides.

intermediates of these bromides may be responsible for the decreased yields.

Subsequently, we carried out the one-pot transformation of different *N*-(2-cyanoaryl)benzamides (Table 2). Four different types of quinazolinones were produced in moderate to good yields by this sequential procedure. The best yield was observed with our model substrate and electron donating substituted examples (Table 2, entries b1 and b2). Substituents in ortho-position to the cyano group did not give any quinazolinone product. This can be explained by the steric hindrance and the suppressed attack of the hydroperoxide anion. Good to excellent yields of quinazolinones can be obtained if the yields are calculated based on the formation of amides. Notably, compared with our previous developed palladium-catalyzed carbonylative synthesis of quinazolinones,[16] the current methodology successfully avoids the manipulation of carbon monoxide gas.

3. Conclusion

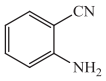
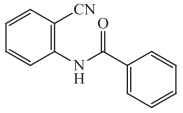
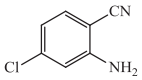
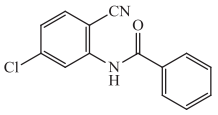
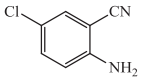
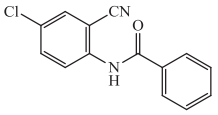
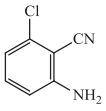
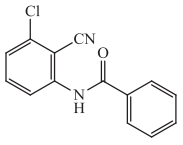
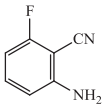
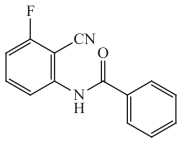
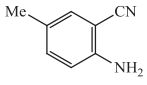
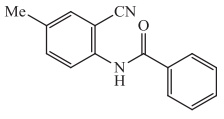
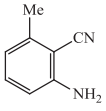
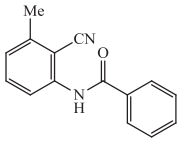
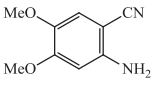
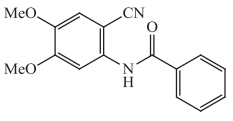
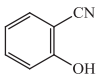
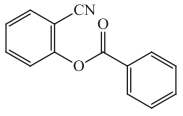
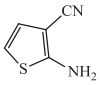
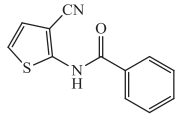
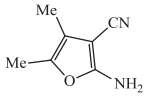
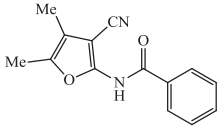
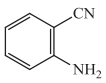
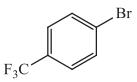
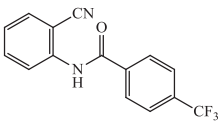
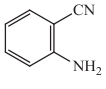
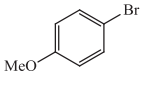
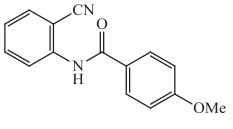
In conclusion, we developed a convenient way to synthesize *N*-(2-cyanoaryl)benzamides from electron withdrawing substituted and steric hindered amines through aminocarbonylation with different bromoarenes. The reactions were carried out using $Mo(CO)_6$ as solid CO source. We showed that these reactions can be carried out with many different weak nucleophilic amines as well as a variety of bromoarenes in 21–92% yields. This methodology does not require special equipment, such as microwave irradiation or autoclaves. Furthermore, we elaborated an advantageous way to synthesize *N*-phenyl-quinazolinones through aminocarbonylation of 2-aminobenzonitriles with bromoarenes and a subsequent oxidant assisted rearrangement in a one-pot manner. Through the presented method, biological interesting heterorganic compounds can be easily prepared.

4. Experimental section

4.1. General

DMF was 99.7% over molecular sieve purchased by Sigma Aldrich. All Chemicals were commercial available and were used without further purification. NMR-data was recorded by a Bruker ARX 300 and Bruker ARX 400 spectrometers. ^{13}C and ^{1}H spectra were referenced to deuterated solvent signals. Peaks were characterized as singlet (s), doublet (d), doublet of doublet (dd), triplet (t), triplet of triplets (tt), quartet (q) and multiplet (m). Gas-chromatographiy-mass-analysis was measured by an Agilent HP-5890 with Agilent HP-5973 Mass Selective Detector (EI) and HP-5-capillary column using helium as carrier gas. Column-chromatographiy was carried out using Merck 60 Silica-Gel (0.043–0.06 mm) and distilled solvents were used.

Table 1
Synthesis of *N*-(2-cyanoaryl)benzamides with $Mo(CO)_6$ as CO-source[a]

Entry	$ArNH_2$	ArBr	Product	Yield[b] (%)
a1				79
a2				0[c]
a3				21
a4				66
a5				92
a6				42
a7				64
a8				71
a9				54
a10				44
a11				50
a12				66
a13				36

(*continued on next page*)

Table 1 (*continued*)

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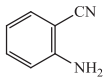
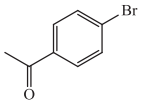
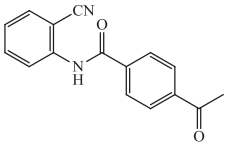
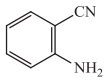
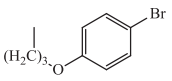
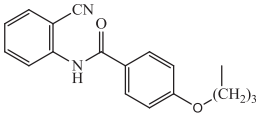
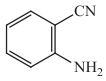
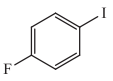
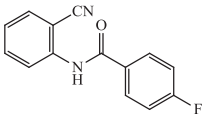
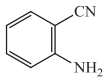
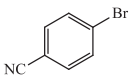
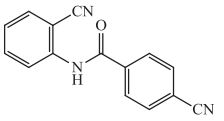
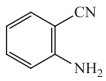
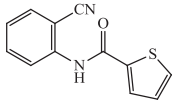
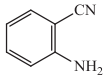
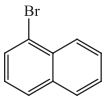
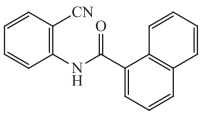
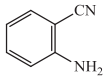
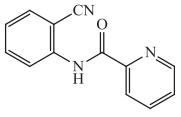
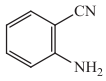
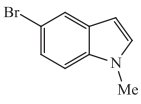
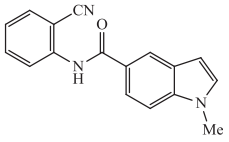
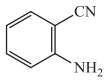
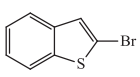
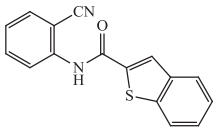
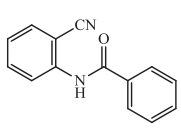
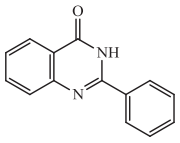
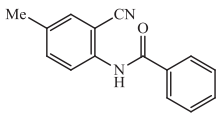
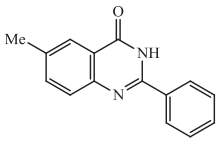
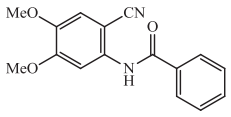
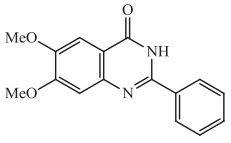
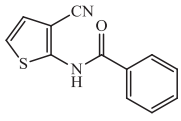
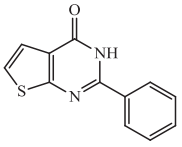
a14				68
a15				31
a16				40
a17				61
a18				39
a19				82
a20				49
a21				61
a22				43

[a] Reaction conditions: 1 equiv amine, 1.2 equiv bromoarene, 0.5 equiv $Mo(CO)_6$, 1.5 equiv DBU, 3 mol % $Pd(OAc)_2$, 6 mol % CataCXium *A*, 4 mL DMF, 130 °C, 16 h.
[b] Isolated yields.
[c] Traces of the desired product been detected in GC/MS.

General procedure for the synthesis of N-(2-cyanoaryl)benzamides from 2-aminobenzonitriles and bromoarenes with Mo(CO)6 as CO source: 1 mmol 2-aminobenzonitrile (118 mg), 1.2 mmol bromobenzene, 6.7 mg $Pd(OAc)_2$ (3 mol %), 21.5 mg CataCXium A (6 mol %), 1.5 mmol DBU (225 μl), 0.5 mmol $Mo(CO)_6$ (132 mg), and 4 mL DMF were given in an argon flushed pressure tube, which was subsequently sealed. The mixture was heated to 130 °C under stirring for 16 h. After cooling to room temperature, the crude mixture was diluted in ethyl acetate and washed with water. The aqueous phase was extracted twice with ethyl acetate. The organic layers were combined, dried over Na_2SO_4, and the solvent was removed under reduced pressure. Column chromatography (hexane/ethyl acetate 8:2) gave 176 mg (79%) *N*-(2-cyanophenyl)benzamide (**a1**) as a white solid. Mp 154–156 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ=10.63 (s, 1H, NH), 8.04–7.97 (m, 2H, CH_{Ar}(9+13)), 7.89 (dd, 1H, ^3J=7.8 Hz, ^4J=1.6 Hz, CH_{Ar}(3)), 7.76 (ddd, 1H, ^3J=7.8 Hz, ^3J=7.8 Hz, ^4J=1.6 Hz, CH_{Ar}(5)), 7.70–7.53 (m, 4H, CH_{Ar}(6+10+11+12)), 7.44 (ddd, 1H, ^3J=7.6 Hz, ^3J=7.6 Hz, ^4J=1.2 Hz, CH_{Ar}(4)) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ=165.7 (C=O(7)), 140.4 (C_{quart}(1)), 133.8 (CH(5)), 133.5 (C_{quart}(8)), 133.1 (CH(3)), 132.2 (CH(11)), 128.6 (CH(10+12)), 127.8 (CH(9+13)), 126.8 (CH(6)), 126.4 (CH(4)), 117.0 (C_{quart}(14)), 109.4 (C_{quart}(2)) ppm; MS (EI, 70 eV): *m*/*z* (%)=222 ([M]$^+$, 23), 105 (100), 77 (52), 51 (15).

General procedure for the synthesis of quinazolinones: To the crude reaction mixture described above was given 1.8 equiv of urea hydrogen peroxide. The mixture was heated to 100 °C under stirring for 7 h. After cooling, 20 mL water was added to precipitate the crude quinazolinone. The solid was filtered off and washed with hexane/ethyl acetate (8:2). The residue was dissolved in the minimum amount of boiling ethyl acetate and recrystallized by the addition of hexane. Filtering gave 170 mg (76%) *N*-phenylquinazolinone (**b1**) as a white solid. Mp 241–243 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ=12.55 (s, 1H, NH), 8.23–8.13 (m, 3H, CH(7+10+14), 7.85 (ddd, ^3J=8.5 Hz, ^3J=7.0 Hz, ^3J=1.6 Hz, CH(5)),

Table 2
Synthesis of quinazolinones from *N*-(2-cyanoaryl)-benzamides[a]

Entry	Amide	Product	Yield[b,c] (%)
b1			76/96
b2			41/98
b3			29/41
b4			25/57

[a] Reaction conditions: 1.8 equiv UHP to the crude solution of the amino-carbonylation, 100 °C, 7 h.
[b] Isolated yields based on amines.
[c] Yields calculated based on amides.

7.77–7.71 (m, 1H, CH(12)), 7.62–7.49 (m, 4H, CH(4+6+11+13)) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ=162.3 (C=O(4)), 152.4 (C_{quart}(2)), 148.7 (C_{quart}(8a)), 134.6 (CH(7)), 132.8 (C_{quart}(9)), 131.4 (CH(12)), 128.6 (CH(10+14)), 127.8 (CH(11+13)), 127.4 (CH(6)), 126.6 (CH(7)), 125.8 (CH(5)), 121.0 (C_{quart}(4a)) ppm; MS (EI, 70 eV): *m*/*z* (%)=222 ([M]$^+$, 100), 119 (99), 104 (11), 92 (14), 90 (17), 77 (22), 76 (11), 51 (10).

*4.1.1. N-(4-Chloro-2-cyanophenyl)benzonitrile (**a3**).* Mp 177–179 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ=10.69 (s, 1H, NH), 8.08 (d, 1H, ^4J=2.5 Hz, CH_{Ar}(3)), 8.02–7.96 (m, 2H, CH_{Ar}(9+13)), 7.83 (dd, 1H, ^3J=8.7 Hz, ^4J=2.5 Hz, CH_{Ar}(5)), 7.69–7.53 (m, 4H, CH_{Ar}(6+10+11+12)) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ=165.6 (C=O(7)), 139.5 (C_{quart}(1)), 133.9 (CH(5)), 133.3 (C_{quart}(8)), 132.5 (CH(3)), 132.3 (CH(11)), 130.1 (C_{quart}(4)), 128.6 (CH(10+12)), 128.3 (CH(6)), 127.9 (CH(9+13)), 115.7 (C_{quart}(14)), 110.7 (C_{quart}(2)) ppm; MS (EI, 70 eV): *m*/*z* (%)=256 ([M]$^+$, 13), 105 (100), 77 (55), 51 (19).

*4.1.2. N-(3-Chloro-2-cyanophenyl)benzonitrile (**a4**).* Mp 163–165 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ=10.79 (s, 1H, NH), 8.03–7.96 (m, 2H, CH_{Ar}(10+14)), 7.77 (dd, 1H, ^3J=8.1 Hz, ^3J=8.1 Hz, CH_{Ar}(5)), 7.70–7.53 (m, 5H, CH_{Ar}(4+6+11+12+13)) ppm; ^{13}C NMR (75 MHz, DMSO): δ=165.7 (C=O(7)), 142.6 (C_{quart}(1)), 135.6 (C_{quart}(3)), 134.7 (CH(5)), 133.2 (C_{quart}(8)), 132.4 (CH(11)), 128.7 (CH(10+12)), 127.9 (CH(9+13)), 126.8 (CH(6)), 125.3 (CH(4)), 114.2 (C_{quart}(14)), 109.9 (C_{quart}(2)) ppm; MS (EI, 70 eV): *m*/*z* (%)=256 ([M]$^+$, 16), 105 (100), 77 (50), 51 (16).

*4.1.3. N-(2-Cyano-3-fluorophenyl)benzonitrile (**a5**).* Mp 167–169 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ=10.81 (s, 1H, NH), 8.05–7.97 (m, 2H, CH_{Ar}(9+13)), 7.81 (ddd, 1H, ^3J=8.4 Hz, ^3J=8.4 Hz, ^4J=6.6 Hz, CH_{Ar}(5)), 7.71–7.35 (m, 5H, CH_{Ar}(4+6+10+11+12)) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ=165.7 (C=O(7)), 162.8 (d, ^1J=254.5 Hz, C_{quart}(3)), 142.0 (d, ^4J=2.5 Hz, (C_{quart}(1)), 135.5 (d, ^3J=10.2 Hz, CH(5)), 133.3 (C_{quart}(8)), 132.4 (CH(11)), 128.7 (CH(9+13)), 128.0 (CH(10+12)), 122.3 (d, ^4J=3.1 Hz, CH(6)), 112.9 (d, ^2J=19.4 Hz, (CH(4)), 112.2 (C_{quart}(14)), 98.38 (d, ^2J=17.2 Hz, (C_{quart}(2)) ppm; MS (EI, 70 eV): *m*/*z* (%)=240 (14), 108 (12), 105 (100), 77 (60), 51 (21).

*4.1.4. N-(2-Cyano-4-methylphenyl)benzonitrile (**a6**).* Mp 204–206 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ=10.52 (s, 1H, NH), 7.99 (dd, 2H, ^3J=8.3 Hz, ^4J=1.5 Hz, CH_{Ar}(10+14)), 7.71–7.68 (m, 1H, CH_{Ar}(3)), 7.67–7.52 (m, 4H, CH_{Ar}(5+11+12+13)), 7.46 (d, 1H, ^3J=8.3 Hz, CH_{Ar}(6)), 2.36 (s, 1H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ=165.7 (C=O(7)), 137.9 (C_{quart}(1)), 136.2 (CH(4)), 134.4 (CH(5)), 133.6 (C_{quart}(8)), 133.0 (CH(3)), 132.1 (CH(11)), 128.6 (CH(10+12)), 127.8 (CH(9+13)), 126.9 (CH(6)), 117.1 (C_{quart}(14)), 109.3 (C_{quart}(2)), 20.1 (CH_3) ppm; MS (EI, 70 eV): *m*/*z* (%)=236 ([M$^+$], 26), 105 (100), 77 (67), 51 (20).

*4.1.5. N-(2-Cyano-3-methylphenyl)benzonitrile (**a7**).* Mp 152–154 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ=10.56 (s, 1H, NH), 8.02–7.97 (m, 2H, CH_{Ar}(10+14)), 7.68–7.51 (m, 4H, CH_{Ar}(5+11+12+13)), 7.41 (d, 1H, ^3J=8.0 Hz, CH_{Ar}(4)), 7.34 (d, 1H, ^3J=7.7 Hz, CH_{Ar}(6)), 2.52 (s, 3H, CH_3) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ=165.7 (C=O(7)), 142.3 (C_{quart}(3)), 140.7 (C_{quart}(1)), 133.7 (C_{quart}(8)), 133.1 (CH(3)), 132.1 (CH(11)), 128.6 (CH(10+12)), 127.8 (CH(9+13)), 127.3 (CH(6)), 124.2 (CH(4)), 115.9 (C_{quart}(2)), 110.1 (C_{quart}(14)), 20.2 (CH_3) ppm; MS (EI, 70 eV): *m*/*z* (%)=236 ([M]$^+$, 28), 105 (100), 77 (65), 51 (20).

*4.1.6. N-(2-Cyano-4,5-dimethoxyphenyl)benzonitrile (**a8**).* Mp 191–193 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ=10.45 (s, 1H, NH), 8.03–7.97 (m, 2H, CH_{Ar}(9+13)), 7.67–7.40 (m, 3H, CH_{Ar}(10+11+12)), 7.40 (s, 1H, CH_{Ar}(3)), 7.16 (s, 1H, CH_{Ar}(6)), 3.84 (s, 3H, CH_3), 3.83 (s, 3H, CH_3) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ=165.6 (C=O(7)), 152.6 (C_{quart}(5)), 146.8 (C_{quart}(4)), 135.2 (C_{quart}(1)), 133.7 (C_{quart}(8)), 132.0 (CH(11)), 130.3 (CH(10+12)), 128.5 (CH(9+13)), 127.7 (CH(3)), 114.2 (C_{quart}(14)), 110.6 (C_{quart}(2)), 100.6 (CH(6)), 56.11 (COMe), 56.0 (COMe) ppm; MS (EI, 70 eV): *m*/*z* (%)=283 (10), 282 ([M]$^+$, 45), 105 (100), 77 (49), 51 (10).

*4.1.7. 2-Cyanophenylbenzoate (**a9**).* Mp 104–106 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ=8.23–8.15 (m, 2H, CH_{Ar}(9+13)), 8.01 (ddd, 1H, ^3J=7.8 Hz, ^4J=1.7 Hz, ^5J=0.5 Hz, CH_{Ar}(3)), 7.92–7.75 (m, 2H, CH_{Ar}(4+5)), 7.72–7.59 (m, 3H, CH_{Ar}(10+11+12)), 7.55 (dd, ^3J=7.6 Hz, ^3J=7.6 Hz, ^2J=1.1 Hz, CH_{Ar}(6)) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ=163.8 (C=O(7)), 152.1 (C_{quart}(1)), 135.2 (CH(5)), 134 (CH(3)), 133.6 (CH(11)), 130.1 (C_{quart}(8)), 129.2 (CH(10+12)), 127.8 (CH(9+13)), 127.2 (CH(4)), 123.8 (CH(6)), 115.2 (C_{quart}(14)), 106.3 (C_{quart}(2)) ppm; MS (EI, 70 eV): *m*/*z* (%)=240 (14), 108 (12), 105 (100), 77 (60), 51 (21).

*4.1.8. N-(3-Cyanothiophen-2-yl)benzamide (**a10**).* Mp 172–174 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ=11.89 (s, 1H), 8.01–7.93 (m, 2H), 7.70–7.63 (m, 1H), 7.62–7.53 (m, 2H), 7.30 (d, ^3J=5.8 Hz, 1H), 7.24 (d, ^3J=5.8 Hz, 1H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ=165.4 (C=O(6)), 152.7 (C_{quart}(2)), 134.9 (C_{quart}(7)); 132.6 (CH(10)), 128.5 (CH(9+11)), 128.4 (CH(8+12)), 125.4 (CH(4)), 120.2 (CH(5)), 114.8 (C_{quart}(13)), 95.4 (C_{quart}(3)) ppm; MS (EI, 70 eV): *m*/*z* (%)=229 ([M]$^+$, 14), 105 (100), 77 (63), 51 (24).

*4.1.9. N-(3-Cyano-4,5-dimethylfuran-2-yl)benzamide (**a11**).* Mp 190–192 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ=11.44 (s, 1H, NH), 8.02–7.97 (m, 2H, CH(8+12)), 7.70–7.62 (m, 1H, CH(10)), 7.56 (ddd, 1H, ^3J=7.5 Hz, ^3J=7.0 Hz, ^3J=1.6 Hz, CH(9+11)), 2.22 (s, 3H, CH_3), 2.01 (s, 3H, CH_3) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ=164.5 (C=O(6)), 149.3 (C_{quart}(5)), 143.0 (C_{quart}(2)), 132.7 (C_{quart}(7)), 132.2 (CH(10)), 128.7 (CH(9+11)), 128.0 (CH(8+12)), 115.2 (C_{quart}(4)), 113.3 (C_{quart}(13)), 88.1 (C_{quart}(3)), 10.8 (CH_3), 8.4 (CH_3) ppm; MS (EI, 70 eV): *m*/*z* (%)=240 ([M]$^+$, 10), 105 (100), 77 (42), 51 (12).

*4.1.10. N-(2-Cyanophenyl)-4-trifluoromethylbenzamide (**a12**).* Mp 189–191 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ=10.88 (s,

1H, NH), 8.23–8.11 (m, 2H, CH(10+12)), 8.03–7.94 (m, 2H, CH(9+13)), 7.91 (ddd, 1H, ^3J=7.8, ^4J=1.6, ^5J=0.5 Hz, CH(3)), 7.77 (ddd, 1H, ^3J=8.1, ^3J=7.5, ^4J=1.6 Hz, CH(5)), 7.61 (ddd, 1H, ^3J=8.2, ^4J=1.2, ^5J=0.5 Hz, CH(6)), 7.47 (ddd, ^3J=7.6, ^3J=7.6 ^3J=1.2 Hz, CH(4)) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ=164.6 (C=O(7)), 139.9 (C_{quart}(1)), 133.8 (CH(5)), 133.2 (CH(8)), 131.9 (q, ^3J=32.0 Hz, CH(10+11)), 128.7 (CH(3)), 126.9 (CH(6)), 126.7 (CH(4)), 125.6 (q, ^4J=3.9 Hz, CH(9+13)), 123.7 (q, ^1J=256.1 Hz, CF_3), 116.8 (C_{quart}(14)), 109.4 (C_{quart}(2)) ppm; MS (EI, 70 eV): *m*/*z* (%)=290 ([M$^+$], 23), 173 (100), 145 (58).

*4.1.11. N-(2-Cyanophenyl)-4-methoxybenzamide (**a13**).* Mp 170–172 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ=10.45 (s, 1H, NH), 8.03–7.96 (m, 2H, CH_{Ar}(9+13)), 7.86 (dd, 1H, ^3J=7.7, ^4J=1.5 Hz, CH_{Ar}(3)), 7.73 (ddd, 1H, ^3J=8.0, ^3J=7.5, ^4J=1.6 Hz, CH_{Ar}(5)), 7.61–7.52 (m, 1H, CH_{Ar}(6)), 7.41 (ddd, 1H, ^3J=7.6, ^3J=7.6, ^4J=1.2 Hz, CH_{Ar}(4)), 7.10 (m, 1H, CH_{Ar}(10+12)), 3.34 (s, 3H, CH_3) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ=165.0 (C=O(7)), 162.3 (C_{quart}(11)), 140.6 (C_{quart}(1)), 133.7 (CH(5)), 133.1 (CH(3)), 129.8 (CH(9+13)), 126.8 (CH(6)), 126.1 (CH(4)), 125.59 (C_{quart}(8)), 117.1 (C_{quart}(14)), 113.81 (CH(10+12)), 109.3 (C_{quart}(2)), 55.51 (CH_3) ppm; MS (EI, 70 eV): *m*/*z* (%)=252 ([M]$^+$, 11), 135 (100), 92 (16), 77 (17), 64 (10).

*4.1.12. 4-Acetyl-N-(2-cyanophenyl)benzamide (**a14**).* Mp 240–242 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ=10.81 (s, 1H, NH), 8.32 (d, 2H, ^3J=8.5 Hz, (CH(10+14)), 8.23–8.07 (m, 2H, (CH(11+13)), 7.91 (dd, ^3J=7.8 Hz, ^4J=1.6 Hz, 1H, CH(3)), 7.82–7.73 (m, 1H, CH(5)), 7.56 (ddd, 1H, ^3J=8.1 Hz, ^3J=7.0 Hz, ^4J=1.3 Hz, CH(4)), 2.65 (s, 3H, CH_3)) ppm; ^{13}C NMR (75 MHz, DMSO): δ=197.7 (C=O(16)), 165.0 (C=O(7)), 140.1 (C_{quart}(2)), 137.3 (C_{quart}(15)), 133.9 (CH(5)), 133.2 (CH(3)), 128.5 (CH(10+14)), 128.2 (CH(11+13)), 126.9 (CH(6)), 126.6 (CH(4)), 116.9 (C_{quart}(15)), 109.4 (C_{quart}(2)), 27.06 (CH_3) ppm; MS (EI, 70 eV): *m*/*z* (%)=264 ([M]$^+$, 22), 147 (100), 104 (14), 91 (19), 76 (17).

*4.1.13. N-(2-Cyanophenyl)-4-pentanoylbenzamide (**a15**).* Mp 148–150 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ=10.80 (s, 1H, NH), 8.13 (m, 4H, CH(9+10+12+13)), 7.90 (dd, 1H, ^3J=7.7 Hz, ^4J=1.5 Hz, CH(3)), 7.85–7.70 (m, 1H, CH(5)), 7.60 (dd, 1H, ^3J=8.2 Hz, ^3J=1.1 Hz, CH(6)), 7.46 (ddd, 1H, ^3J=7.6 Hz, ^3J=7.6 Hz, ^3J=1.2 Hz, CH(4)), 3.09 (t, 1H, ^3J=7.2 Hz, H_2(16)), 1.73–1.54 (m, 2H, CH_2(17)), 1.38 (m, 2H, CH_2(18)), 0.92 (t, ^3J=7.3 Hz, 3H, CH_3(19)) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ=199.9 (C=O(15)), 164.9 (C=O(7)), 140.0 (C_{quart}(1)), 139.2 (C_{quart}(11)), 137.06 (C_{quart}(8)), 133.8 (CH(5)), 133.1 (CH(3)), 128.1 (CH(9+13)), 128.0 (CH(10+12)), 126.9 (CH(6)), 126.6 (CH(4)), 116.8 (C_{quart}(14)), 109.4 (C_{quart}(2)), 38.0 (CH_2(16)), 25.8 (CH_2(17)), 21.7 (CH_2(18)), 13.8 (CH_3(19)) ppm; MS (EI, 70 eV): *m*/*z* (%)=306 ([M]$^+$, 28), 264 (11), 249 (14), 147 (18), 104 (29), 76 (19).

*4.1.14. N-(2-Cyanophenyl)-4-fluorobenzamide (**a16**).* Mp 185–187 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ=10.66 (s, 1H), 8.12–8.04 (m, 2H), 7.88 (dd, *J*=7.8, 1.5 Hz, 1H), 7.75 (ddd, *J*=8.1, 7.5, 1.6 Hz, 1H), 7.58 (dd, *J*=8.2, 1.1 Hz, 1H), 7.48–7.37 (m, 3H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ=164.6 (C=O(7)), 164.42 (d, ^1J=249.8 Hz, CF(11)), 140.2 (C_{quart}(1)), 133.8 (CH(5)), 133.1 (CH(3)), 130.6 (d, ^3J=9.3 Hz, CH(9+13)), 130.0 (d, ^4J=3.0 Hz, C_{quart}(8)), 126.9 (CH(6)), 126.5 (CH(4)), 117.0 (C_{quart}(14)), 115.6 (d, ^2J=21.9 Hz, CH(10+12)), 109.4 (C_{quart}(2)) ppm; MS (EI, 70 eV): *m*/*z* (%)=240 ([M]$^+$, 18), 123 (100), 95 (48), 75 (21).

*4.1.15. N-(2-Cyanophenyl)-4-cyanobenzamide (**a17**).* Mp 228–230 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ=10.89 (s, 1H, NH), 8.15 (d, 2H, ^3J=8.3 Hz, CH(9+13)), 8.07 (d, 2H, ^3J=8.2 Hz, CH(10+12)), 7.91 (dd, 1H, ^3J=7.6 Hz, ^4J=1.6 Hz, CH(3)), 7.77 (ddd, 1H, ^3J=7.7 Hz, ^4J=1.6 Hz, CH(5)), 7.60 (d, 1H, ^3J=8.1 Hz, CH(6)), 7.47 (ddd, ^3J=7.7 Hz, ^4J=1.3 Hz, CH(4)) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ=164.4 (C=O(7)), 139.9 (C_{quart}(1)), 137.5 (CH(5)), 133.9 (C_{quart}(9)), 133.2 (CH(3)), 132.7 (CH(9+13)), 128.6 (CH(10+12)), 126.9 (CH(6)), 126.8 (CH(4)), 118.2 (C_{quart}(15)), 116.8 (C_{quart}(14), 114.4 (C_{quart}(12)), 109.4 (C_{quart}(2)) ppm; MS (EI, 70 eV): *m*/*z* (%)=247 ([M]$^+$, 25), 130 (100), 102 (51), 75 (14).

*4.1.16. N-(2-Cyanophenyl)thiophene-2-carboxamide (**a18**).* Mp 134–136 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ=10.64 (s, 1H, NH), 8.02 (dd, 1H ^3J=3.8 Hz, ^4J=1.2 Hz, 1H, CH(9)), 7.92 (dd, 1H, ^3J=5.0 Hz, ^4J=1.1 Hz, CH(11)), 7.90–7.86 (m, 1H (CH(3)), 7.75 (ddd, 1H, ^3J=8.2 Hz, ^3J=7.5 Hz, ^4J=1.6 Hz, CH(5)), 7.57 (m, 1H, CH(6)), 7.44 (ddd, 1H, ^3J=7.6 Hz, ^3J=7.6 Hz, ^4J=1.2 Hz, (CH4)), 7.27 (dd, 1H, ^3J=5.0 Hz, ^4J=3.7 Hz CH(10)) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ=160.1 (C=O(7)), 139.8 (C_{quart}(1)), 138.5 (C_{quart}(8)), 133.8 (CH(5)), 133.2 (CH(3)), 132.5 (CH(9)), 129.9 (CH(11)), 128.2 (CH(10)), 126.9 (CH(6)), 126.5 (CH(4)), 116.9 (C_{quart}(12)), 109.3 (C_{quart}(2)) ppm; MS (EI, 70 eV): *m*/*z* (%)=228 ([M$^+$], 23), 111 (100), 39 (20).

*4.1.17. N-(2-Cyanophenyl)-1-naphthamide (**a19**).* Mp 159–161 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ=10.88 (s, 1H, NH), 8.40–8.32 (m, 1H, CH(16)), 8.12 (ddd, 1H, ^3J=8.4 Hz, ^3J=8.4 Hz, ^4J=1.0 Hz, CH(11)), 8.07–8.00 (m, 1H, CH(13)), 7.92 (dd, 1H, ^3J=7.7 Hz, ^3J=1.5 Hz, CH(9)), 7.87 (dd, 1H, ^3J=7.2 Hz, ^4J=1.2 Hz, CH(3)), 7.83–7.74 (m, 1H, CH(5)), 7.69–7.57 (m, 4H, CH(6+9+14+15)), 7.47 (ddd, 1H, ^3J=7.6 Hz, ^3J=7.6 Hz, ^3J=1.2 Hz, CH(4)) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ=167.7 (C=O(7)), 140.1 (C_{quart}(1)), 134.0 (CH(5)), 133.4 (C_{quart}(8)), 133.3 (CH(3)), 133.3 (C_{quart}(12)), 130.8 (CH(11)), 129.8 (C_{quart}(17)), 128.4 (CH(13)), 127.2 (CH(14)), 126.8 (CH(6)), 126.6 (CH(9)), 126.6 (CH(4)), 126.0 (CH(10)), 125.3 (CH(15)), 125.1 (CH(13)), 117.2 (C_{quart}(18)), 109.3 (C_{quart}(2)) ppm; MS (EI, 70 eV): *m*/*z* (%)=272 ([M]$^+$, 19), 155 (100), 127 (77), 126 (16).

*4.1.18. N-(2-Cyanophenyl)picolinamide (**a20**).* Mp 126–128 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ=10.92 (s, 1H, NH), 8.78 (ddd, 1H, ^3J=4.8 Hz, ^4J=1.7 Hz, ^5J=0.9 Hz, (CH9)), 8.25–8.16 (m, 1H, CH(12)), 8.12 (dd, 1H, ^3J=7.6 Hz, ^4J=1.7 Hz, CH(11)), 8.07 (m, 1H, CH(10)), 7.89 (dd, 1H, ^3J=7.8 Hz, ^4J=1.6 Hz, CH(3)), 7.84–7.68 (m, 2H (CH(5+6)), 7.39 (ddd, 1H, ^3J=7.6 Hz, ^3J=7.6 Hz, ^3J=1.1 Hz, CH(4)) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ=162.5 (C=O(7)), 148.7 (C_{quart}(8)), 148.7 (CH(9)), 140.0 (C_{quart}(1)), 138.4 (CH(11)), 134.1 (CH(5)), 133.0 (CH(3)), 127.6 (CH(6)), 125.5 (CH(4)), 123.8 (CH(10)), 122.6 (CH(12)), 116.6 (C_{quart}(13)), 105.9 (C_{quart}(2)) ppm; MS (EI, 70 eV): *m*/*z* (%)=223 ([M]$^+$, 69), 106 (30), 90 (17), 79 (99), 78 (100), 76 (100), 63 (11), 52 (31), 51 (32), 50 (12).

*4.1.19. N-(2-Cyanophenyl)-1-methyl-1H-indole-5-carboxamide (**a21**).* Mp 165–167 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ=10.47 (s, 1H, NH), 8.31 (d, 1H, ^4J=1.6 Hz, CH(13)), 7.92–7.80 (m, 2H, CH(3+10)), 7.74 (ddd, 1H, ^3J=8.1 Hz, ^3J=7.5 Hz, ^4J=1.6 Hz, CH(5)), 7.60 (m, 2H (CH(6+9), 7.47 (d, 1H, ^4J=3.1 Hz, CH(11)), 7.41 (ddd, 1H, ^3J=7.6 Hz, ^3J=7.6 Hz, ^4J=1.2 Hz, (CH(4)), 6.62 (dd, 1H, ^3J=3.1 Hz, ^4J=0.8 Hz, CH(12)), 3.86 (s, CH_3) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ=166.4 (C=O(7)), 141.0 (C_{quart}(1)), 138.2 (C_{quart}(10a)), 133.6 (CH(5)), 133.0 (CH(3)), 131.4 (C_{quart}(12a)), 129.3 (C_{quart}(8)), 127.3 (CH(11)), 126.6 (CH(6)), 125.8 (C_{quart}(8)), 121.1 (CH(10)), 121.0 (CH(13)), 117.1 (C_{quart}(14)), 109.5 (CH(9)), 109.0 (C_{quart}(2)), 101.7 (CH(12)), 32.67 (CH_3) ppm; MS (EI, 70 eV): *m*/*z* (%)=275 ([M]$^+$, 21), 159 (11), 158 (100), 130 (28), 103 (13), 77 (15).

*4.1.20. N-(2-Cyanophenyl)benzo[b]thiophene-2-carboxamide (**a22**).* Mp 164–166 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ=10.69 (s, 1H, NH), 8.65 (s, 1H, CH(13)), 8.48–8.43 (m, 1H, CH(9)), 8.13–8.09 (m, 1H, (CH(12)), 7.90 (ddd, 1H, ^3J=7.7 Hz, ^4J=1.6 Hz, ^5J=0.5 Hz, (CH3)), 7.77 (ddd, 1H, ^3J=8.1 Hz, ^3J=7.5 Hz, ^4J=1.6 Hz, CH(5)), 7.61 (ddd, 1H, ^3J=8.1 Hz, ^4J=1.2 Hz, ^5J=0.5 Hz, CH(6)), 7.51–7.44 (m, 3H, (CH(4+10+11)) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ=161.9 (C=

O(7)), 148.2 (C_{quart}(8)), 140.0 (C_{quart}(1)), 139.5 (C_{quart}(9a)), 136.9 (C_{quart}(12a)), 133.8 (CH(5)), 133.1 (CH(3)), 126.5 (CH(6)), 126.2 (CH(4)), 125.1 (CH(11)), 125.1 (CH(10)), 124.5 (CH(12)), 124.3 (CH9)), 122.9 (CH(13)), 117.0 (C_{quart}(14)), 109.1 (C_{quart}(2)) ppm; MS (EI, 70 eV): *m*/*z* (%)=278 ([M]$^+$, 21), 162 (11), 161 (100), 133 (20), 90 (10), 89 (38).

*4.1.21. 6-Methyl-2-phenylquinazolin-4(3H)-one (**b5**).* Mp 262–264 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ=12.47 (s, 1H, NH), 8.20–8.13 (m, 2H, CH(10+14)), 7.95 (d, ^4J=1.9 Hz, 1H, (CH(5))), 7.66–7.64 (m, 2H, CH(7+8)), 7.59–7.50 (m, 3H, CH(11+12+13)), 2.46 (s, 3H, CH_3) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ=162.2 (C=O(4)), 151.5 (C_{quart}(2)), 146.8 (C_{quart}(8a)), 136.3 (C_{quart}(6)), 135.90 (C_{quart}(9)), 132.9 (CH(7)), 131.2 (CH(12)), 128.6 (CH(11+13)), 127.6 (CH(10+14)), 127.4 (CH(5)), 125.3 (CH(8)), 120.7 (CH(4a)), 20.9 (CH_3) ppm; MS (EI, 70 eV): *m*/*z* (%)=237 (18), 236 ([M]$^+$, 100), 133 (81), 105 (13), 104 (40), 89 (12), 78 (13), 77 (47), 76 (13), 51 (19).

*4.1.22. 6,7-Dimethoxy-2-phenylquinazolin-4(3H)-one (**b7**).* Mp 290–292 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ=12.42 (s, 1H, NH), 8.23–8.11 (m, 2H, CH(10+14)), 7.59–7.50 (m, 3H, CH(11+12+13)), 7.49 (s, 1H, CH(5)), 7.22 (s, 1H, CH(8)), 3.94 (s, 3H, CH_3), 3.90 (s, 3H, CH_3) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ=161.6 (C=O(4)), 154.8 (C_{quart}(8a)), 150.8 (C_{quart}(9)), 148.6 (C_{quart}(7)), 144.8 (C_{quart}(6)), 132.8 (C_{quart}(9)), 131.0 (CH(12)), 128.6 (CH(11+13)), 127.4 (CH(9+14)), 114.0 (C_{quart}(4a)), 108.3 (CH(8)), 104.9 (CH(5)), 56.0 (CH_3), 55.7 (CH_3) ppm; MS (EI, 70 eV): *m*/*z* (%)=283 (16), 282 ([M]$^+$, 100), 281 (20), 268 (12), 267 (47), 239 (24), 237 (16), 104 (19), 32 (11).

*4.1.23. 2-Phenylthieno[2,3-d]pyrimidin-4(3H)-one (**b9**).* Mp 233–235 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ=13.44 (s, 1H, NH), 7.93 (m, 2H, CH(5+6)), 7.65 (m, 5H, CH(10+11+12+13+14)) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ=167.4 (CH(6)), 162.5 (C=O(4)), 146.2 (C_{quart}(2)), 132.7 (C_{quart}(7)), 132.1 (CH(10)), 129.3 (CH(8+12)), 127.0 (CH(9+11)), 123.2, 116.5 (C_{quart}(6a)), 115.7 (C_{quart}(4a)) ppm; MS (EI, 70 eV): *m*/*z* (%)=229 ([M]$^+$, 32), 105 (100), 77 (82), 51 (24), 50 (11).

Acknowledgements

The authors thank the state of Mecklenburg-Vorpommern and the Bundesministerium für Bildung und Forschung (BMBF) for financial support. We also thank Drs. W. Baumann, C. Fischer, Ms. S. Schareina and Ms. S. Buchholz (LIKAT) for analytical support.

Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.11.055.

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