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Rapid access to benzo-annelated heterocycles, naphthalenes, and polysubstituted benzenes through a novel benzannulation reaction

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ABSTRACT

A novel, efficient, and powerful methyl mercaptoacetate triggered benzannulation reaction is described. The precursors are heterocyclic, aromatic or acyclic compounds bearing a carbonyl group at *ortho* position to an internal alkyne. The methodology does not require transition-metal catalysts and moreover it is general for the preparation of wide range of benzo-annelated heterocycles, naphthalenes and benzenes.

1. Introduction

Benzannulation is an important process in organic synthesis since a wide range of organic molecules contains fused benzene rings. Since the pioneering work of Berthelot,[1] a variety of synthetic methodologies for the creation of new benzene rings have been developed, starting from acyclic or cyclic precursors.[2] Benzannulation processes can be divided into two large groups: first would be transition-metal mediated processes, such as the chromium-assisted [3+2+1] Dötz cycloaddition, first reported in 1975.[3] This reaction involves an α,β-unsaturated carbene ligand, an alkyne and a carbonyl ligand within the coordination sphere of a chromium(0) metal center and leads to the formation of highly substituted aromatic compounds. Palladium-catalyzed two-component [4+2] and three-component [2+2+2] benzannulations have also been widely studied.[4] The next group comprises transition-metal catalyzed reactions is the ruthenium-mediated[5] or cobalt-mediated [2+2+2] cyclotrimerizations of alkynes,[6] and Lewis acidic metal catalyzed processes.[5a,7] Thirdly, metal free methods comprising electrophilic cyclization using ICl or $I(Py)_2BF_4$,[8] benzannulation under ultraviolet irradiation,[9] via acidic conditions,[10] base-induced processes[11] and aminobenzannulations.[12]

Recently, we have discovered straightforward metal-free methyl mercaptoacetate triggered [4+2] benzannulations of starting 6-arylethynylpyrimidine-5-carbaldehydes and 2-arylethynylquinoline-3-carbaldehydes. Highly concise and high-yielding methods for the preparation of quinazolines and acridines were described.[13] We became interested in widening the application of our method for the synthesis of a variety of benzo-annelated compounds. Therefore, we report herein the details of our recent investigations.

2. Results and discussion

For the synthesis of starting compounds, bearing a formyl group and ethynyl moiety in close proximity, we utilized a classical Sonogashira coupling[14] between halogen derivatives and terminal acetylenes. Thus, we prepared 2,4-disubstituted 6-alkynylpyrimidine-5-carbaldehydes (**1**–**10**),[15] 6-substituted-2-phenylethynylquinoline-3-carbaldehydes (**11**–**14**),[16] 2-alkynylindole-3-carbaldehydes (**15**–**17**),[17] 2-alkynylbenzofurane-3-carbaldehydes (**18**–**19**),[12b] 2-alkynylthiophene-3-carbaldehydes (**20**–**23**), 3,4-dialkoxy-2-alkynylbenzaldehydes (**24**–**28**),[18] and 3-phenyl-2(*Z*)-penten-4-ynals (**29**–**30**) (Fig. 1).[19]

After we had prepared the requisite heteroaryl and aryl substrates, bearing formyl group and alkynyl substituent in close proximity to each other, we could then test their reactivity toward our methyl mercaptoacetate triggered benzannulation. First of all, we explored the scope of benzannulation of pyrimidine substrates (**1**–**10**) (Table 1). As we have previously described,[13a] 2,4-disubstituted 6-phenylethynylpyrimidine-5-carbaldehydes underwent a smooth benzannulation reaction with the potassium salt

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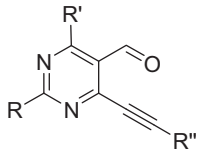

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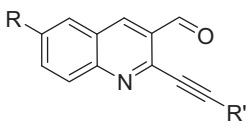

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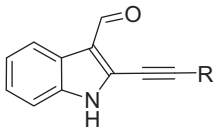

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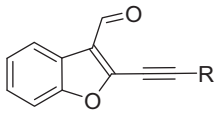

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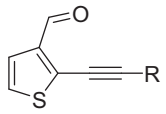

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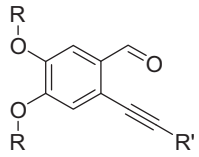

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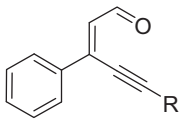
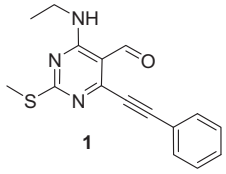
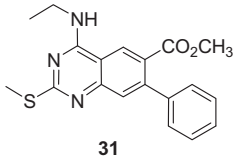
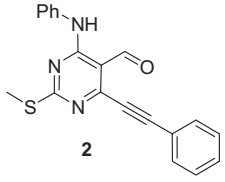
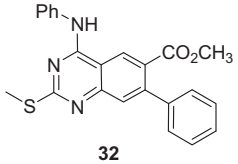
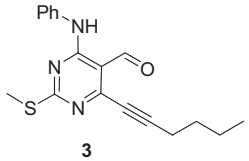
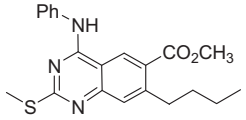
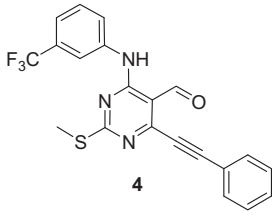
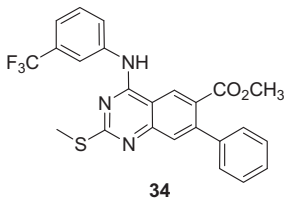


29-30

1: R = SCH_3; R' = NHC_2H_5; R'' = C_6H_5; **2**: R = SCH_3; R' = NHC_6H_5; R'' = C_6H_5; **3**: R = SCH_3; R' = NHC_6H_5; R'' = C_4H_9; **4**: R = SCH_3; R' = NH(3-$CF_3C_6H_4$); R'' = C_6H_5; **5**: R = SCH_3; R' = NH(3-BrC_6H_4); R'' = C_6H_5; **6**: R = SCH_3, R' = $N(CH_2)_4$; R'' = C_6H_5; **7**: R = SCH_3; R' = $N(CH_2)_4O$; R'' = C_6H_5; **8**: R = $NHCH_2CH{=}CH_2$; R' = NH(3-Br-C_6H_4); R'' = C_6H_5; **9**: R = $NHCH_2CH{=}CH_2$, R' = NH(3-$CF_3C_6H_4$); R'' = C_6H_5; **10**: R = $N(CH_2)_4O$; R' = NH(3-$CF_3C_6H_4$); R'' = C_6H_5; **11**: R = R' = H; **12**: R = H, R' = C_6H_5; **13**: R = OCH_3, R' = C_6H_5; **14**: R = OC_2H_5, R' = C_6H_5; **15**: R = C_6H_5; **16**: R = 4-$CH_3C_6H_4$; **17**: 4-$C_2H_5C_6H_4$; **18**: R = $Si(CH_3)_3$; **19**: R = C_6H_5; **20**: R = C_6H_5; **21**: R = 4-$C_2H_5C_6H_4$; **22**: R = $Si(CH_3)_3$; **23**: R = C_4H_9; **24**: R = CH_3, R' = H; **25**: R = CH_3, R' = $Si(CH_3)_3$; **26**: R = CH_3, R' = C_6H_5; **27**: 2R = CH_2; R' = $Si(CH_3)_3$; **28**: 2R = CH_2; R' = C_6H_5; **29**: R = $Si(CH_3)_3$; **30**: R = C_6H_5.

Fig. 1. Precursors for the benzannulation reactions.

Table 1
Benzannulation products: quinazolines from 4-ethynylpyrimidine-5-carbaldehydes

Starting compound	Product	Method[a]	Yield %
 **1**	 **31**	A B	87 89
 **2**	 **32**	A C	98 98
 **3**	 **33**	C	81
 **4**	 **34**	B C	56 79

(*continued on next page*)

Table 1 (*continued*)

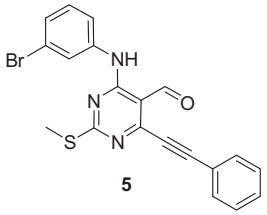
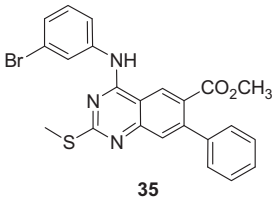
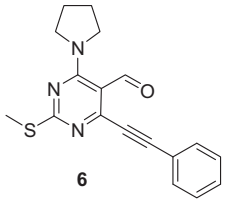
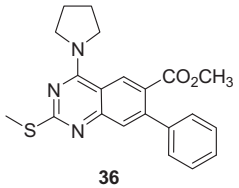
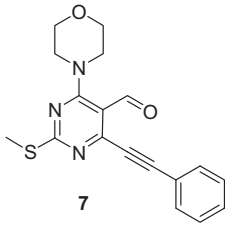
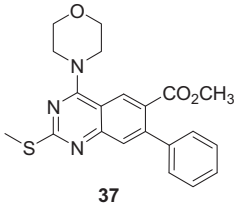
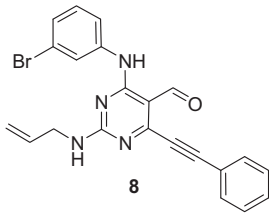
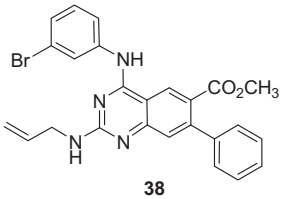
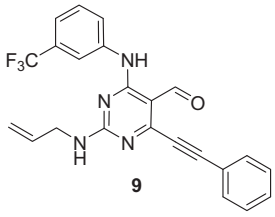
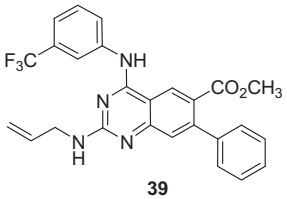
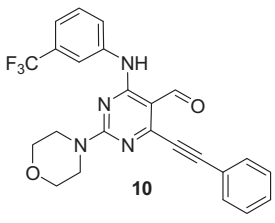
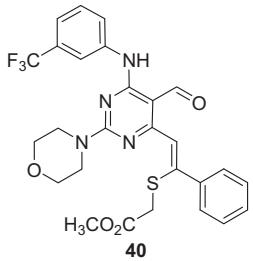
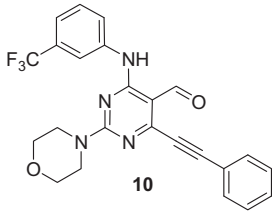
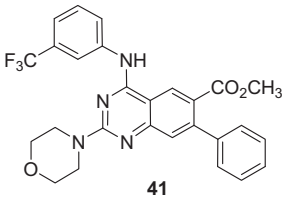
Starting compound	Product	Method[a]	Yield %
 **5**	 **35**	C	80
 **6**	 **36**	A B C	86 87 95
 **7**	 **37**	A C	85 90
 **8**	 **38**	C	65
 **9**	 **39**	C	71
 **10**	 **40**	B	48

Table 1 (*continued*)

Starting compound	Product	Method[a]	Yield %
 **10**	 **41**	C	86

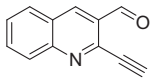
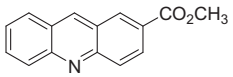
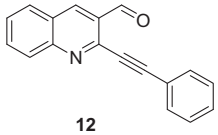
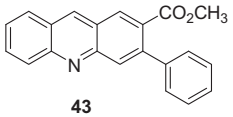
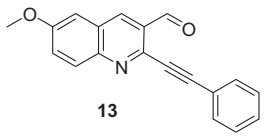
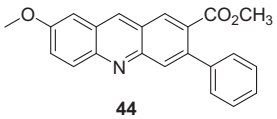
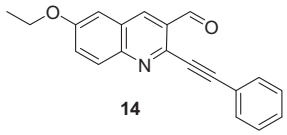
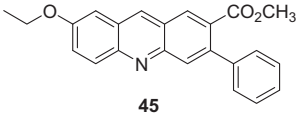
[a] Method A: A solution of starting compound (1 equiv), methyl mercaptoacetate (1 equiv), and 1.1 equiv of potassium *tert*-butanolate in methanol was mixed at room temperature for 2–4 h. Method B: A solution of starting compound (1 equiv), methyl mercaptoacetate (1 equiv), and 1.1 equiv of potassium *tert*-butanolate in methanol was refluxed for 2–4 h. Method C: A solution of starting compound (1 equiv), methyl mercaptoacetate (1 equiv), and 1.1 equiv of potassium *tert*-butanolate in methanol was irradiated in a microwave oven at 440 W for 2–10 min.

of methyl mercaptoacetate in methanol and high-yielding formation of quinazolines were observed. It is noteworthy, that in case of insoluble starting materials, the reaction rate is diminished leading to decreased yield of the target compound. Heating the reaction mixture in methanol moderately increased the yields for the benzannulation for 2-methylthio-6-phenylethynylpyrimidine-5-carbaldehydes **1**,**2**,**4**–**6**. However, those substrates bearing a bulky *N*,*N*-dialkylamino substituent in the position 2 of the pyrimidine ring afforded only complex mixtures. In the case of substrate **10**, we isolated the intermediate of the benzannulation reaction—the product of conjugate addition of methyl mercaptoacetate to triple bond **40**.[20] In order to solve this problem; we decided to take advantage of microwave-assisted chemistry. To our pleasant surprise, when solutions of compounds **1**–**9** and potassium salt of methyl mercaptoacetate in methanol were irradiated in a microwave oven, after 1–3 min the high-yielding formation of quinazolines **31**–**39** and **41** took place. In these cases, the substituents in positions 2 and 4 of the pyrimidine ring did not have any effect.

Analogously, we prepared acridine derivatives **42** - **45**. The cyclization occurred rapidly and was complete in 3 min after irradiation of the reaction mixtures in a microwave oven (440 W) (Table 2).

At this stage of the investigation, it appeared that activation of the triple bond by the electron-withdrawing pyrimidine or quinoline nucleus played an important role in enabling a successful and regioselective nucleophilic addition of methyl mercaptoacetate to the C≡C moiety and following benzannulation. Nevertheless, we decided to examine the generality of our method and turned our attention to electron rich substrates (e.g., indole, benzofuran, and

Table 2
Benzannulation products: acridines from 2-ethynylquinoline-3-carbaldehydes[a]

Starting compound	Product	Method[a]	Yield %
 **11**	 **42**	B C	48 76
 **12**	 **43**	A C	90 99
 **13**	 **44**	A C	51 75
 **14**	 **45**	C	51

[a] Method A: A solution of starting compound (1 equiv), methyl mercaptoacetate (1 equiv), and 1.1 equiv of potassium *tert*-butanolate in methanol was mixed at room temperature for 2–4 h. Method B: A solution of starting compound (1 equiv), methyl mercaptoacetate (1 equiv), and 1.1 equiv of potassium *tert*-butanolate in methanol was refluxed for 2–4 h. Method C: A solution of starting compound (1 equiv), methyl mercaptoacetate (1 equiv), and 1.1 equiv of potassium *tert*-butanolate in methanol was irradiated in a microwave oven at 440 W for 2–10 min.

benzene derivatives). To our pleasant surprise, the starting compounds bearing electron-donating heterocycle indole **15**–**17** reacted with the potassium salt of methyl mercaptoacetate in methanol and formed the desired carbazoles **46**–**48** in high yields after irradiation of reaction mixtures in a microwave oven for 3–5 min. Moreover it is noteworthy, that there was no need to protect the *NH* moiety on indole ring (something, that is, usually recommended under basic reaction conditions). Analogously, the one-step benzannulation reaction was suitable for the preparation of dibenzofuran derivatives **49**, **50** and benzo[*b*]thiophenes **51**–**54**. In the case of 2-trimethylsilylethynylbenzo[*b*]furan-3-carbaldehyde **18** and 2-trimethylsilylethynylthiophene-3-carbaldehyde **22**, cyclization occurred together with the concomitant loss of the TMS group (Table 3).

And finally, the heterocyclic moiety can be changed to a simple benzene ring or suitable acyclic substrate. Table 4 summarizes the short and convenient synthetic protocol for polysubstituted naphthalenes and biphenyls. The benzannulation reaction took from 2 to 10 min in a microwave oven at 440 W.

Moreover, we performed the same experiment with methyl 2-ethynylbenzenecarboxylates **61** and **63**[21] and we obtained methyl 1-hydroxynaphthalene-2-carboxylates **62** and **64** in moderate yields.

The present benzannulation process is believed to proceed via an antiaromatic thiepine **I** as outlined in Scheme 1. We suppose that during the reaction of starting compounds with potassium salt of methyl mercaptoacetate the conjugated nucleophilic addition to C≡C moiety together with Dieckmann type condensation took place and intermediated **I** formed. Intermediates **I** due to their anti-aromaticity underwent smooth 1,6-electrocyclic ring closure (intermediates **II**) and following aromatization with elimination of sulfur to form the corresponding benzo-annelated heterocycles, naphtalenes, and benzenes. Analogous transformation from benzothiepine to naphthalene derivatives was reported earlier,[22] so our proposed mechanism seems to be reasonable. Unfortunately, we did not succeed to isolate antiaromatic thiepines **I** from the reaction mixtures. But on the other hand, another intermediate methyl (*Z*)-2-[5-formyl-2-morpholino-6-(3-trifluoromethylanilino)-4-pyrimidinyl-1–phenylethenyl]thioacetate **40** after the resubmission to the reaction conditions also formed the final benzoannelated product **41**. The only one logical speculation about the latter result can be intramolecular condensation of intermediates **III** to form thiepines **I** and following rearrangements as described above. Moreover, it should be noted that during running reactions at a higher scale (≥1 g. of starting material), the precipitation of elemental sulfur can be observed easily.

It is noteworthy that methyl mercaptoacetate is the most efficient reagent for this transformation. Other thiols, such as 1-butanethiol and benzylthiol did not trigger the benzannulation process. The unique role of mercaptoacetic acid ester is due to active methylene group and also due to soft nucleophilicity of thiole moiety.

3. Conclusion

Overall, the development of methyl mercaptoacetate triggered benzannulation leads to the synthesis of attractive quinazolines, acridines, carbazoles, dibenzofurans, benzo[*b*]thiophenes, naphthalenes, and polysubstituted benzenes. Our methodology allows the construction of aromatic carboxylic acid derivatives in a newly formed ring. The reaction does not require metal-catalysts and moreover—it is really unique method of the synthesis of benzo-annelated heterocycles, since the key step is formation of benzene ring instead of usual heterocyclic ring formation. We believe that our developed methodology can be applied for the synthesis of variety of important aromatic compounds.

4. Experimental section

4.1. General

Melting points were determined in open capilliaries and are uncorrected. IR spectra were run in Nujol mulls or in KBr discs on a Perkin–Elmer FT spectrophotometer Spectrum BX II. ^{1}H and ^{13}C NMR spectra were recorded with a Varian Unity INOVA spectrometer (300 MHz) using tetramethylsilane as internal standard. Elemental analyses (C, N, H) results were found to be in good agreement (±0.4%) with the calculated values. All reactions and the purity of the synthesized compounds monitored by TLC using Silica gel 60 F_{254} aluminum plates (Merck). Visualization was accomplished by UV light.

4.2. General procedure for the Sonogashira reaction

A mixture of the appropriate aryl halide (5 mmol), $PdCl_2(PPh_3)_2$ (5 mol %), and Et_3N (1.01 g; 10 mmol) was suspended in anhydrous THF (8 mL). Then the appropriate acetylene (1.1 equiv) was injected under argon, followed by addition of CuI (2.5 mol %). The reaction mixture was stirred under argon at 40 °C temperature until full completion (normally 1–3 h, completion observed by TLC). Solvent was evaporated under the reduced pressure; the crude residue was purified by column chromatography (elution by mixtures of toluene and ethylacetate).

Data for compounds **1**–**2**,[15b] **6**–**7**,[15a] **11**–**13**,[16a] **15**,[17] **18**–**19**,[12b] **24**–**26**,[18] **29**–**30**,[19] have been published previously.

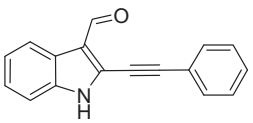
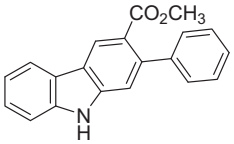
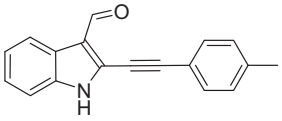
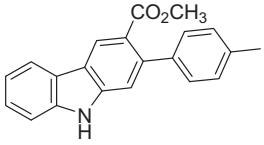
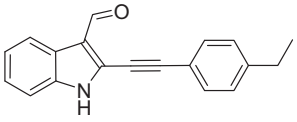
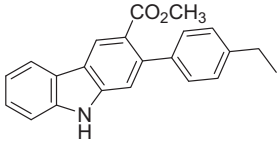
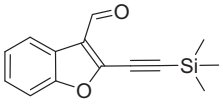
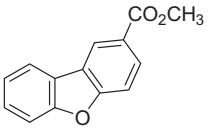
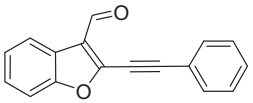
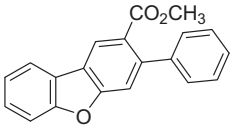
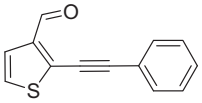
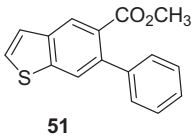
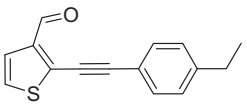
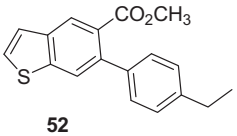
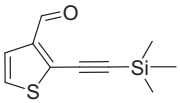
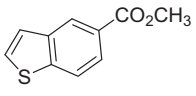
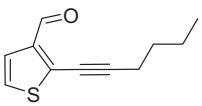
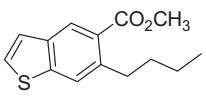
4.2.1. 6-Anilino-4-(1-hexynyl)-2-methylthiopyrimidine-5-carbaldehyde ***3***. Yellowish crystals, yield 75%, mp 85–87 °C. IR (KBr): ν_{max}=3139 (NH), 2239 (C≡C), 1648 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.98 (3H, t, J=7.5 Hz, $CH_2CH_2CH_2CH_3$), 1.44–1.52 (2H, m, $CH_2CH_2CH_2CH_3$), 1.63–1.73 (2H, m, $CH_2CH_2CH_2CH_3$), 2.55 (2H, t, J=7.2 Hz, $CH_2CH_2CH_2CH_3$), 2.57 (3H, s, SCH_3), 7.19 (1H, tt, J=8.4; 0.9 Hz, ArH), 7.39 (2H, t, J=8.4 Hz, ArH), 7.71–7.74 (2H, m, ArH), 10.38 (1H, s, CHO), 11.05 (1H, br s, NH) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=13.3, 14.4, 19.2, 21.9, 29.7, 75.5, 101.4, 108.3, 121.9, 124.6, 128.6, 137.1, 155.5, 156.9, 177.4, 191.9 ppm. Anal. Calcd for $C_{18}H_{19}N_3OS$: C, 66.43; H, 5.88; N, 12.91. Found: C, 66.54; H, 5.93; N, 13.00.

4.2.2. 2-Methylthio-6-phenylethynyl-4-(3-trifluoromethylanilino)pyrimidine-5-carbaldehyde ***4***. Yellowish crystals, yield 74%, mp 174–176 °C (from 2-PrOH). IR (KBr): ν_{max}=3409 (NH), 2213 (C≡C), 1647 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.63 (3H, s, SCH_3), 7.45–7.53 (5H, m, ArH), 7.67–7.70 (3H, m, ArH), 8.44 (1H, br s, ArH), 10.55 (1H, s, CHO), 11.27 (1H, br s, NH) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=14.6, 83.4, 98.7, 108.4, 119.1 (q, J=3.75 Hz), 120.4, 121.2 (q, J=4.5 Hz), 127.7 (q, J=12.75 Hz), 128.0 (q, J=72.75 Hz), 128.7, 129.4, 130.6, 131.4, 132.6, 137.9, 155.3, 157.3, 178.3, 191.9 ppm. Anal. Calcd for $C_{21}H_{14}F_3N_3OS$: C, 61.01; H, 3.41; N, 10.16. Found: C, 61.19; H, 3.25; N, 10.22.

4.2.3. 4-(3-Bromoanilino)-2-methylthio-6-phenylethynylpyrimidine-5-carbaldehyde ***5***. Yellowish crystals, yield 76%, mp 186–188 °C (from DMF). IR (KBr): ν_{max}=3428 (NH), 2213 (C≡C), 1644 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.65 (3H, s, SCH_3), 7.24–7.34 (2H, m, ArH), 7.42–7.50 (4H, m, ArH), 7.66–7.69 (2H, m, ArH), 8.28 (1H, br s, ArH), 10.52 (1H, s, CHO), 11.13 (1H, br s, NH) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=14.8, 83.5, 98.7, 108.4, 120.3, 120.4, 122.4, 125.2, 127.6, 128.7, 130.1, 130.5, 132.5, 138.6, 155.3, 157.1, 178.1, 191.9 ppm. Anal. Calcd for $C_{20}H_{14}BrN_3OS$: C, 56.61; H, 3.33; N, 9.90. Found: C, 56.39; H, 3.21; N, 9.92.

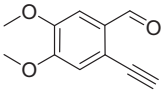
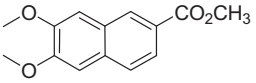
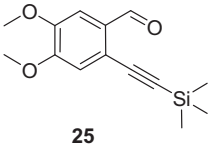
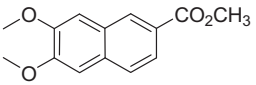
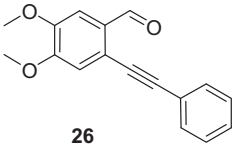
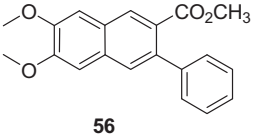
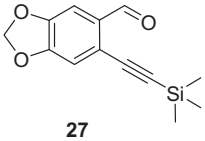
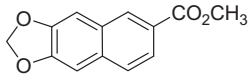
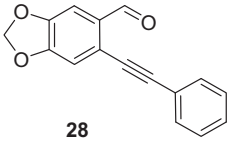
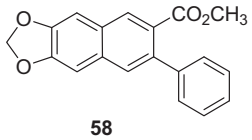
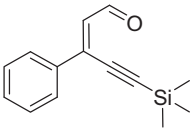
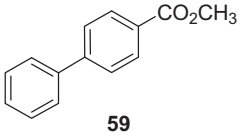
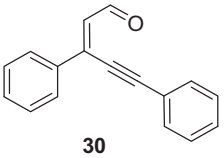
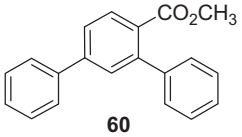
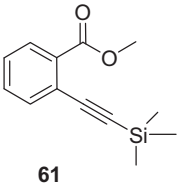
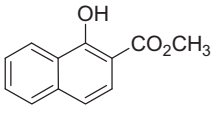
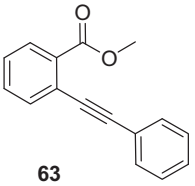
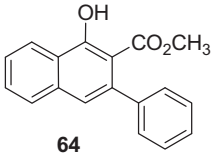
4.2.4. 6-Ethoxy-2-phenylethynylquinoline-3-carbaldehyde ***14***. Yellowish crystals, yield 65%, mp 175 °C (from 2-PrOH). IR (KBr):

Table 3
Benzannulation products: carbazoles, dibenzofuranes and benzo[*b*]thiophenes from 2-ethynylindole-3-carbaldehydes, 2-ethynylbenzo[*b*]furane-3-carbaldehydes and 2-ethynylthiophene-3-carbaldehydes[a]

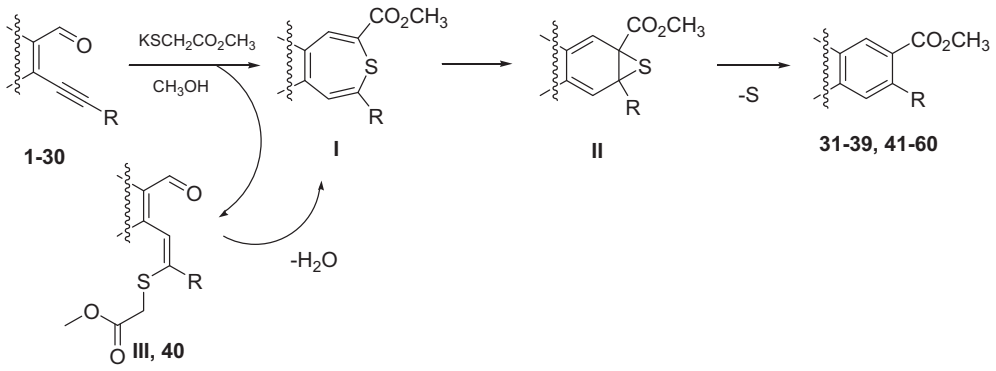
Starting compound	Product	Yield %
 **15**	 **46**	80
 **16**	 **47**	62
 **17**	 **48**	79
 **18**	 **49**	66
 **19**	 **50**	70
 **20**	 **51**	60
 **21**	 **52**	64
 **22**	 **53**	78
 **23**	 **54**	81

[a] All reaction were run in domestic microwave oven at 440 W for 2–10 min using 1 equiv of starting compound, 1 equiv of methyl mercaptoacetate, 1.1 equiv of potassium *tert*-butanolate in methanol.

Table 4
Benzannulation products: naphthalenes and biphenyls from 2-alkynylbenzaldehydes and 3-phenyl-2(*E*)-penten-4-ynals[a]

Starting compound	Product	Yield %
 **24**	 **55**	79
 **25**	 **55**	90
 **26**	 **56**	88
 **27**	 **57**	98
 **28**	 **58**	81
 **29**	 **59**	70
 **30**	 **60**	65
 **61**	 **62**	55
 **63**	 **64**	39

[a] All reaction were run in domestic microwave oven at 440 W for 2–10 min using 1 equiv of starting compound, 1 equiv of methyl mercaptoacetate, 1.1 equiv of potassium *tert*-butanolate in methanol.



Scheme 1. Possible mechanism for the benzannulation reactions.

ν_{max}=2212 (C≡C), 1692 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=1.45 (3H, t, J=6.9 Hz, OCH_2CH_3), 4.10 (2H, q, J=6.9 Hz, OCH_2CH_3), 7.04 (1H, d, J=2.7 Hz, C_5–H), 7.37–7.45 (4H, m, ArH), 7.64–7.67 (2H, m, ArH), 7.99 (1H, d, J=9.3 Hz, C_8–H), 8.48 (1H, s., C_4–H), 10.70 (1H, s, CHO) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=14.5, 63.9, 85.5, 94.4, 106.6, 121.4, 126.3, 127.5, 128.3, 128.7, 129.4, 130.4, 132.0, 135.0, 141.0, 146.2, 158.1, 190.7 ppm. Anal. Calcd for $C_{20}H_{15}NO_2$: C, 79.73; H, 4.98; N, 4.65. Found: C, 79.82; H, 5.28; N, 4.61.

4.2.5. 2-(4-Methylphenylethynyl)-1H-indole-3-carbaldehyde ***16***. Yellowish crystals, yield 55%, mp 174–176 °C (from octane). IR (KBr): ν_{max}=3175 (NH), 2210 (C≡C), 1636 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=2.37 (3H, s, CH_3), 7.25–7.36 (4H, m, ArH), 7.48 (1H, d, J=8.1 Hz, C_7–H), 7.60 (2H, d, J=8.1 Hz, ArH), 8.14 (1H, d, J=7.8 Hz, C_4–H), 10.22 (1H, s, CHO), 12.75 (1H, br s, NH) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=21.1, 78.2, 97.4, 111.9, 117.5, 119.2, 120.7, 122.9, 123.9, 124.8, 128.9, 129.5, 131.6, 136.2, 139.9, 184.3 ppm. Anal. Calcd for $C_{18}H_{13}NO$: C, 83.37; H, 5.05; N, 5.40. Found: C, 83.57; H, 5.36; N, 5.56.

4.2.6. 2-(4-Ethylphenylethynyl)-1H-indole-3-carbaldehyde ***17***. Yellowish crystals, yield 59%, mp 134–136 °C (from octane). IR (KBr): ν_{max}=3180 (NH), 2210 (C≡C), 1636 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=1.29 (3H, t, J=7.5 Hz, CH_2CH_3), 2.71 (2H, q, J=7.5 Hz, CH_2CH_3), 7.24 (2H, d, J=8.4 Hz, ArH), 7.32–7.36 (2H, m, C_5–H, C_6–H), 7.40–7.44 (1H, m, C_7–H), 7.50 (2H, d, J=8.4 Hz, ArH), 8.33–8.37 (1H, m, C_4–H), 9.27 (1H, br s, NH), 10.33 (1H, s, CHO) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=15.2, 28.9, 77.7, 98.6, 111.1, 118.3, 120.5, 121.9, 123.4, 124.4, 125.2, 128.2, 129.7, 131.8, 135.8, 146.5, 185.7 ppm. Anal. Calcd for $C_{19}H_{15}NO$: C, 83.49; H, 5.53; N, 5.12. Found: C, 83.27; H, 5.72; N, 5.14.

4.2.7. 2-Phenylethynylthiophene-3-carbaldehyde ***20***. Yellow oil, yield 63%. IR (KBr): ν_{max}=2205 (C≡C), 1667 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=7.24–7.26 (1H, m, C_4–H), 7.38–7.41 (3H, m, ArH), 7.44 (1H, d, J=5.4 Hz, C_5–H), 7.54–7.58 (2H, m, ArH), 10.17–10.19 (1H, m, CHO) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=79.3, 100.3, 121.7, 125.1, 127.0, 128.6, 129.5, 131.6, 134.6, 142.8, 184.7 ppm. Anal. Calcd for $C_{13}H_8OS$: C, 73.56; H, 3.80. Found: C, 73.58; H, 3.97.

4.2.8. 2-(4-Ethylphenylethynylthiophene-3-carbaldehyde) ***21***. Yellow oil, yield 70%. IR (KBr): ν_{max}=2205 (C≡C), 1680 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=1.24 (3H, t, J=7.8 Hz, CH_3), 2.66 (2H, q, J=7.8 Hz, CH_2), 7.19–7.23 (3H, m, C_4–H, and ArH), 7.42 (1H, dd, J=5.4, 0.3 Hz, C_5–H), 7.47 (2H, d, J=8.4 Hz, ArH), 10.18 (1H, dd, J=0.5, 0.3 Hz, CHO) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=15.2, 28.8, 78.7, 100.7, 118.7, 124.9, 126.7, 128.1, 131.6, 134.9, 142.5, 146.1, 184.6 ppm. Anal. Calcd for $C_{15}H_{12}OS$: C, 74.97; H, 5.03. Found: C, 75.00; H, 4.91.

4.2.9. 2-Trimethylsilylethynylthiophene-3-carbaldehyde ***22***. Yellow oil, yield 82%. IR (KBr): ν_{max}=2147 (C≡C), 1687 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=0.26 (9H, s, $Si(CH_3)_3$), 7.19 (1H, dd, J=4.8, 1.2 Hz, C_4–H), 7.44 (1H, d, J=4.8, 0.3 Hz, C_5–H), 10.19 (1H, dd, J=1.2, 0.3 Hz, CHO) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=−0.45, 93.6, 107.3, 124.8, 126.9, 134.3, 143.5, 184.7 ppm. Anal. Calcd for $C_{10}H_{12}OSSi$: C, 57.65; H, 5.81. Found: C, 57.72; H, 5.99.

4.2.10. 2-(1-Hexynyl)thiophene-3-carbaldehyde ***23***. Yellow oil, yield 78%. IR (KBr): ν_{max}=2223 (C≡C), 1682 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=0.93 (3H, t, J=7.5 Hz, $CH_2CH_2CH_2CH_3$), 1.41–1.49 (2H, m, $CH_2CH_2CH_2CH_3$), 1.55–1.63 (2H, m, $CH_2CH_2CH_2CH_3$), 2.49 (2H, t, J=7.2 Hz, $CH_2CH_2CH_2CH_3$), 7.10 (1H, dd, J=5.4, 0.9 Hz, C_4–H), 7.34 (1H, dd, J=5.4, 0.3 Hz, C_5–H), 10.0.3 (1H, dd, J=0.9, 0.3 Hz, CHO) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=13.5, 19.5, 21.9, 30.2, 70.8, 102.8, 124.6, 125.7, 136.0, 142.4, 184.8 ppm. Anal. Calcd for $C_{11}H_{12}OS$: C, 68.71; H, 6.29. Found: C, 68.68; H, 6.35.

4.2.11. 6-Trimethylsilylethynyl-1,3-benzodioxole-5-carbaldehyde ***27***. White crystals, yield 85%, mp 124–125 °C. IR (KBr): ν_{max}=2213 (C≡C), 1689 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=0.29 (9H, s, $Si(CH_3)_3$), 6.10 (2H, s, OCH_2O), 6.98 (1H, s, ArH), 7.35 (1H, s, ArH), 10.41 (1H, s, CHO) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=−0.2, 99.9, 101.0, 102.3, 105.9, 112.3, 123.4, 132.6, 148.8, 152.2, 190.2 ppm. Anal. Calcd for $C_{13}H_{14}O_3Si$: C, 63.39; H, 5.73. Found: C, 63.44; H, 5.78.

4.2.12. 6-Phenylethynyl-1,3-benzodioxole-5-carbaldehyde ***28***. White crystals, yield 66%, mp 121–122 °C (from 2-PrOH). IR (KBr): ν_{max}=2211 (C≡C), 1685 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=6.12 (2H, s, OCH_2O), 7.06 (1H, s, ArH), 7.39–7.42 (4H, m, ArH), 7.55–7.58 (4H, m, ArH), 10.51 (1H, s, CHO) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=84.7, 95.1, 102.4, 106.1, 111.9, 122.3, 123.6, 128.5, 128.9, 131.5, 132.1, 148.7, 152.4, 189.9 ppm. Anal. Calcd for $C_{16}H_{10}O_3$: C, 76.79; H, 4.03. Found: C, 76.85; H, 3.95.

4.3. General procedure for the preparation of compounds 8–10

To a solution of starting 4-substituted 2-methylthio-6-phenylethynylpyrimidine-5-carbaldehyde (1.6 mmol) in dichloromethane (20 mL), *m*-chloroperbenzoic acid was added (0.41 g, 2.4 mmol) in portions. The resulting solution was mixed for 3 h at rt, then the corresponding amine (4.8 mmol) was added. The reaction mixture was mixed for 8 h at rt, then washed with sodium bicarbonate (satd

aq, 75 mL), brine (3×30 mL), dried over anhydrous sodium sulfate, filtered and concentrated in vacuo to give compounds **8**–**10**.

*4.3.1. 4-(3-Bromoanilino)-6-phenylethynyl-2-(2-propenylamino)pyrimidine-5-carbaldehyde **8***. Yellowish crystals, yield 50%, mp 184–186 °C (from 2-PrOH). IR (KBr): ν_{max}=3348, 3236 (NH), 2211 (C≡C), 1632 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=4.15–4.19 (2H, m, CH_2), 5.23 (1H, dd, J=13.8; 1.2 Hz, =CH), 5.33 (1H, dd, J=17.1; 1.2 Hz, =CH), 5.94–6.07 (1H, m, =CH), 6.24 (1H, t, J=5.7 Hz, NH), 7.20–7.26 (2H, m, ArH), 7.41–7.50 (4H, m, ArH), 7.64–7.67 (2H, m, ArH), 8.29 (1H, br s, ArH), 10.33 (1H, s, CHO), 11.24 (1H, br s, NH) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=43.9, 83.7, 96.8, 106.1, 116.4, 119.9, 122.3, 124.8, 126.9, 128.6, 129.9, 130.0, 130.2, 132.4, 133.6, 139.4, 157.5, 159.5, 161.9, 189.8 ppm. Anal. Calcd for $C_{22}H_{17}BrN_4O$: C, 60.98; H, 3.95; N, 12.93. Found: C, 61.26; H, 3.91; N, 13.00.

*4.3.2. 6-Phenylethynyl-2-(2-propenylamino)-4-(3-trifluoromethylanilino)pyrimidine-5-carbaldehyde **9***. Yellowish crystals, yield 66%, mp 184–186 °C (from 2-PrOH). IR (KBr): ν_{max}=3309, 3243 (NH), 2211 (C≡C), 1629 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=4.16–4.19 (2H, m, CH_2), 5.22 (1H, dd, J=10.2; 1.2 Hz, =CH), 5.30 (1H, dd, J=17.85; 1.2 Hz, =CH), 5.92–6.05 (1H, m, =CH), 6.12 (1H, t, J=1.2 Hz, NH), 7.39–7.52 (6H, m, ArH), 7.66–7.69 (2H, m, ArH), 8.47 (1H, br s, ArH), 10.35 (1H, s, CHO), 11.37 (1H, br s, NH) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=43.9, 83.5, 97.1, 106.0, 116.2, 118.7 (q, J=5.0 Hz), 120.5, 124.3 (q, J=12.8 Hz), 128.6 (q, J=101.0 Hz), 129.2, 129.9, 130.1, 130.3, 130.9, 132.4, 133.3, 138.6, 157.3, 159.6, 161.7, 189.8 ppm. Anal. Calcd for $C_{23}H_{17}F_3N_4O$: C, 65.40; H, 4.06; N, 13.26. Found: C, 65.29; H, 4.23; N, 13.17.

*4.3.3. 2-Morpholino-6-phenylethynyl-4-(3-trifluoromethylanilino)pyrimidine-5-carbaldehyde **10***. Yellowish crystals, yield 64%, mp 176–178 °C (from 2-PrOH). IR (KBr): ν_{max}=3436 (NH), 2215 (C≡C), 1632 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=3.80–3.83 (4H, m, $N(CH_2)_2$), 3.94 (2H, br s, OCH_2), 4.08 (2H, br s, OCH_2), 7.39–7.52 (5H, m, ArH), 7.58–7.61 (1H, m, ArH), 7.67 (2H, dd, J=8.1, 1.5 Hz, ArH), 8.41 (1H, br s, ArH), 10.35 (1H, s, CHO), 11.24 (1H, br s, NH) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=44.6, 66.8, 84.2, 96.5, 105.7, 118.8 (q, J=3.75 Hz), 120.4 (q, J=3.75 Hz), 120.8, 128.6, 129.2, 129.7, 130.1 (q, J=32.3 Hz), 130.2, 132.4, 132.4, 138.6, 157.5, 159.2, 160.6, 189.9 ppm. Anal. Calcd for $C_{24}H_{19}F_3N_4O_2$: C, 63.71; H, 4.23; N, 12.38. Found: C, 63.89; H, 4.21; N, 12.19.

4.4. General method for the benzannulation reaction

To a solution of the corresponding starting material (0.3 mmol) in methanol (5 mL) a solution of potassium salt of methyl mercaptoacetate, prepared from potassium (11.7 mg, 0.3 mmol), methyl mercaptoacetate (31.8 mg, 0.3 mmol), and methanol (3 ml) was added. The resulting reaction mixture was irradiated in close 15 mL vessel in domestic microwave oven (model DAEWOO KOR6305A) at 440 W for 2–10 min. After the completion of the reaction (observed by TLC), the solvent was evaporated under the reduced pressure, the residue redissolved in dichloromethane (15 mL), washed with 5% sodium bicarbonate solution (3×15 mL), then with brine (2×15 mL) and finally with water (2×15 mL). The organic layer was dried over magnesium sulfate, filtered and evaporated. The residue was purified by column chromatography (mixture of cyclohexane and ethylacetate).

*4.4.1. 4-Ethylamino-6-methoxycarbonyl-2-methylthio-7-phenylquinazoline **31***. White crystals, yield 89% mp 110–112 °C (from methanol). IR (KBr): ν_{max}=3345 (NH), 1701 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=1.41 (3H, t, J=7.2 Hz, CH_3), 2.66 (3H, s, SCH_3), 3.68 (3H, s, OCH_3), 3.73–3.82 (2H, m, CH_2), 5.82 (1H, br s, NH), 7.36–7.46 (5H, m, ArH), 7.71 (1H, s, CH), 8.26 (1H, s, CH) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=14.1, 14.5, 36.4, 52.1, 111.0, 124.6, 126.4, 127.6, 128.0 (2C); 128.1, 128.8, 140.5, 146.5, 151.6, 158.3, 168.2 ppm. Anal. Calcd for $C_{19}H_{19}N_3O_2S$: C, 64.57; H, 5.42; N, 11.89. Found: C, 64.39; H, 5.48; N, 12.00.

*4.4.2. 4-Anilino-6-methoxycarbonyl-2-methylthio-7-phenylquinazoline **32***. White crystals, yield 98% mp 177–179 °C (from octane). IR (KBr): ν_{max}=3386 (NH), 1707 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=2.65 (3H, s, SCH_3), 3.69 (3H, s, OCH_3), 7.23 (1H, tt, J=7.5, 0.9 Hz, ArH), 7.38–7.48 (7H, m, ArH), 7.67 (1H, br s, NH), 7.74 (1H, s, CH), 7.83 (2H, dd, J=8.5, 1.2 Hz, ArH), 8.44 (1H, s, CH) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=14.3, 52.2, 111.1, 121.7, 124.5, 124.6, 127.2, 127.7, 128.0, 128.1, 128.9, 129.0, 137.8, 140.2, 146.7, 151.9, 156.3, 168.4, 171.1 ppm. Anal. Calcd for $C_{23}H_{19}N_3O_2S$: C, 68.81; H, 4.77; N, 10.47. Found: C, 69.00; H, 4.89; N, 10.37.

*4.4.3. 4-Anilino-7-butyl-6-methoxycarbonyl-2-methylthioquinazoline **33***. Yellowish crystals, yield 81%, mp 101–103 °C (from methanol). IR (KBr): ν_{max}=3384 (NH), 1721 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=0.93 (3H, t, J=7.2 Hz, $CH_2CH_2CH_2CH_3$), 1.33–1.46 (2H, m, $CH_2CH_2CH_2CH_3$), 1.55–1.65 (2H, m, $CH_2CH_2CH_2CH_3$), 2.59 (3H, s, SCH_3), 3.05 (2H, t, J=7.8 Hz, $CH_2CH_2CH_2CH_3$), 3.93 (3H, s, OCH_3), 7.16 (1H, tt, J=7.5, 1.2 Hz, ArH), 7.39 (2H, td, J=7.5, 1.2 Hz, ArH), 7.53 (1H, s, ArH), 7.76 (2H, dd, J=7.5, 1.2 Hz, ArH), 7.79 (1H, br s, NH), 8.47 (1H, s, ArH) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=13.9, 14.2, 22.7, 33.3, 34.5, 52.2, 110.3, 121.7, 124.6, 125.3, 125.5, 126.2, 128.2, 128.9, 137.8, 149.4, 156.4, 167.2, 170.8 ppm. Anal. Calcd for $C_{21}H_{23}N_3O_2S$: C, 66.12; H, 6.08; N, 11.01. Found: C, 66.21; H, 5.98, N, 12.95.

*4.4.4. 6-Methoxycarbonyl-2-methylthio-7-phenyl-4-(3-trifluoromethylanilino)quinazoline **34***. White crystals, yield 79% mp 186–188 °C (from octane). IR (KBr): ν_{max}=3372 (NH), 1713 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=2.67 (3H, s, SCH_3), 3.71 (3H, s, OCH_3), 7.37–7.49 (6H, m, ArH), 7.58 (1H, t, J=8.1 Hz, ArH), 7.76 (1H, s, CH), 7.84 (1H, br s, NH), 7.90–7.94 (1H, m, ArH), 8.35 (1H, m, ArH), 8.46 (1H, s, CH) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=14.3, 52.3, 110.8, 118.4 (q, J=3.5 Hz), 121.0 (q, J=3.75 Hz), 124.2, 126.0, 127.6, 127.9, 128.1, 128.2, 129.2, 129.5, 130.1 (q, J=34.0 Hz), 132.6, 138.4, 140.0, 147.1, 151.9, 156.2, 168.2, 170.4 ppm. Anal. Calcd for $C_{24}H_{18}F_3N_3O_2S$: C, 61.40; H, 3.86; N, 8.95. Found: C, 61.82; H, 3.71; N, 9.00.

*4.4.5. 4-(3-Bromomethylanilino)-6-methoxycarbonyl-2-methylthio-7-phenylquinazoline **35***. White crystals, yield 80% mp 204–205 °C (from 2-PrOH). IR (KBr): ν_{max}=3370 (NH), 1728 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=2.68 (3H, s, SCH_3), 3.69 (3H, s, OCH_3), 7.33–7.46 (7H, m, ArH), 7.68 (1H, dt, J=7.5, 2.1 Hz, ArH), 7.73 (1H, br s, NH), 7.74 (1H, s, CH), 8.23 (1H, t, J=2.1 Hz, ArH), 8.42 (1H, s, CH) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=14.4, 52.3, 110.9, 119.7, 122.5, 124.2, 124.5, 125.1, 127.4, 127.9, 128.1, 128.2, 129.2, 130.2, 139.1, 140.1, 146.9, 152.0, 156.1, 168.3, 171.1 ppm. Anal. Calcd for $C_{23}H_{18}BrN_3O_2S$: C, 57.51; H, 3.78; N, 8.75. Found: C, 57.27; H, 3.68; N, 8.91.

*4.4.6. 6-Methoxycarbonyl-2-methylthio-7-phenyl-4-pyrrolidinoquinazoline **36***. White crystals, yield 95% mp 185–187 °C (from methanol). IR (KBr): ν_{max}=1708 (C=O) cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ=2.01 (4H, br s, $(CH_2)_2$), 2.54 (3H, s, SMe), 3.62 (3H, s, OMe), 3.92 (4H, br s, $N(CH_2)_2$), 7.37–7.47 (5H, m, ArH), 7.45 (1H, s, CH), 8.64 (1H, s, CH) ppm. ^{13}C NMR (75 Hz, DMSO-d_6): δ=13.4, 25.0, 50.6, 51.9, 11.9, 125.0, 127.2, 127.6, 127.9, 128.1, 129.2, 139.7, 144.8, 152.9, 157.5, 167.4, 168.7 ppm. Anal. Calcd for $C_{21}H_{21}N_3O_2S$: C, 66.47; H, 5.58; N, 11.07. Found: C, 66.37; H, 5.53; N, 11.11. Crystal structure analysis for **36**: $C_{21}H_{21}N_3O_2S$, M_r=379.47 g mol^{-1}, monoclinic, space group P 21/*a*, *a*=7.5916(2), *b*=19.0791(4), *c*=13.2219(4) Å, α=90.00, β=94.3120(9), γ=90.00 °, V=1909.65(9) $Å^3$, ρ=1.320 g/cm^3, *F*(000)=800. Crystallographic data for structure

36 have been deposited at the Cambridge Crystallographic Data Centre (CCDC number 703429).

4.4.7. 6-Methoxycarbonyl-2-methylthio-4-morpholino-7-phenylquinazoline ***37***. White crystals, yield 90% mp 154–156 °C (from octane). IR (KBr): ν_{max}=1717 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=2.64 (3H, s, SCH_3), 3.68 (3H, s, OCH_3), 3.93 (8H, s, N(CH_2)$_4$O), 7.39–7.45 (5H, m, ArH), 7.74 (1H, s, CH), 8.37 (1H, s, CH) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=14.2, 49.9, 52.2, 66.6, 112.0, 126.3, 127.7, 128.0, 128.1, 128.4, 128.8, 140.3, 146.2, 153.9, 163.1, 168.1, 169.7 ppm. Anal. Calcd for $C_{21}H_{21}N_3O_3S$: C, 63.78; H, 5.35; N, 10.63. Found: C, 63.75; H, 5.34; N, 10.77.

4.4.8. 4-(3-Bromomethylanilino)-6-methoxycarbonyl-7-phenyl-2-(2-propenylamino)quinazoline ***38***. White crystals, yield 65% mp 215–217 °C (from methanol). IR (KBr): ν_{max}=3370, 3079 (NH), 1706 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=2.61 (1H, br s, NH), 3.67 (3H, s, OCH_3), 4.17–4.20 (2H, m, CH_2), 5.20 (1H, dd, J=10.2, 1.2 Hz, =CH), 5.32 (1H, dd, J=17.1, 1.2 Hz, =CH), 5.98–6.10 (1H, m, =CH), 7.27–7.35 (5H, m, ArH), 7.40–7.46 (3H, m, ArH), 7.41 (1H, s, CH), 7.61 (1H, d, J=7.5 Hz, ArH), 8.19 (1H, br s, NH), 8.39 (1H, s, CH) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=43.9, 52.0, 116.0, 119.8, 122.5, 123.8, 124.5, 124.9, 127.2, 127.6, 127.9, 128.1, 128.4, 129.0, 130.1, 134.8, 139.4, 140.7, 147.2, 157.9, 159.7, 161.4, 168.3 ppm. Anal. Calcd for $C_{25}H_{21}BrN_4O_2$: C, 61.36; H, 4.33; N, 11.45. Found: C, 61.58; H, 4.31; N, 11.55.

4.4.9. 6-Methoxycarbonyl-7-phenyl-2-(2-propenylamino)-4-(3-trifluoromethylanilino)-quinazoline ***39***. White crystals, yield 71% mp 229–230 °C (from methanol). IR (KBr): ν_{max}=3362, 3076 (NH), 1700 (C=O) cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ=3.62 (3H, s, OCH_3), 4.01–4.03 (2H, m, CH_2), 5.07 (1H, dd, J=10.2, 1.2 Hz, =CH), 5.19 (1H, dd, J=17.1, 1.2 Hz, =CH), 5.92–6.02 (1H, m, =CH), 7.35–7.46 (7H, m, ArH), 7.24 (1H, s, CH), 7.62 (1H, t, J=8.1 Hz, ArH), 8.18 (1H, br s, NH), 8.51–8.62 (1H, m, ArH), 8.88 (1H, s, CH), 10.08 (1H, br s, NH) ppm. ^{13}C NMR (75 Hz, DMSO-d_6): δ=43.0, 51.7, 109.6, 119.4 (q, J=3 Hz), 122.4, 122.9, 125.2, 125.9, 126.6 (q, J=3 Hz), 127.4, 127.8, 128.1, 128.9, 129.3, 129.4, 130.2 (q, J=38.0 Hz), 135.9, 140.2, 140.4, 145.5, 145.6, 153.7, 167.8, 171.9 ppm. Anal. Calcd for $C_{26}H_{21}F_3N_4O_2$: C, 65.27; H, 4.42; N, 11.71. Found: C, 65.33; H, 4.39; N, 11.66.

4.4.10. Methyl (Z)-2-[5-formyl-2-morpholino-6-(3-trifluoromethylanilino)-4-pyrimidinyl-1-phenyl-ethenyl]thioacetate ***40***. Yellow crystals, yield 48% mp 181–182 °C (from methanol). IR (KBr): ν_{max}=3369 (NH), 1723, 1641 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=3.14–3.18 and 3.38–3.41 (4H, 2 m, N(CH_2)$_2$), 3.54 (2H, s, SCH_2), 3.64–3.66 and 3.74–3.75 (4H, 2 m, O(CH_2)$_2$), 3.79 (3H, s, OCH_3), 7.06 (1H, s, CH), 7.31–7.36 (6H, m, ArH), 7.45 (1H, t, J=8.4 Hz, ArH), 7.54 (1H, d, J=8.1 Hz, ArH), 8.36 (1H, br s, ArH), 10.16 (1H, s, CHO), 11.40 (1H, br s, NH) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=34.5, 43.8, 44.3, 52.8, 66.5, 66.7, 102.9, 118.3, 118.6 (q, J=4.5 Hz), 120.0 (q, J=3.75 Hz), 124.3, 128.4, 128.6, 129.0, 129.1, 129.8 (q, J=40 Hz), 130.6, 131.0, 137.5, 138.9, 150.2, 159.9, 167.9, 169.3, 188.1 ppm. Anal. Calcd for $C_{27}H_{25}F_3N_4O_4S$: C, 58.06; H, 4.51; N, 10.03. Found: C, 58.13; H, 4.66; N, 9.96.

4.4.11. 6-Methoxycarbonyl-2-morpholino-7-phenyl-4-(3-trifluoromethylanilino)quinazoline ***41***. White crystals, yield 86% mp 179–180 °C (from methanol). IR (KBr): ν_{max}=3369 (NH), 1711 (C=O) cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ=3.63 (3H, s, OCH_3), 3.67–3.70 (4H, m, N(CH_2)$_2$), 3.78–3.80 (4H, m, O(CH_2)$_2$), 7.35–7.49 (6H, m, ArH), 7.32 (1H, s, CH), 7.65 (1H, t, J=8.1 Hz, ArH), 8.06 (1H, d, J=8.1 Hz, ArH), 8.38 (1H, br s, ArH), 8.89 (1H, s, CH), 10.29 (1H, br s, NH) ppm. ^{13}C NMR (75 Hz, DMSO-d_6): δ=44.1, 51.7, 65.8, 108.8, 118.4 (q, J=3.75 Hz), 119.6 (q, J=3 Hz), 123.7, 125.4, 126.1, 126.5, 127.5, 127.8, 128.0, 129.5, 132.2 (q, J=35.75 Hz), 139.7, 140.2, 145.7, 153.1, 157.9, 158.5167.7, 171.8 ppm. Anal. Calcd for $C_{27}H_{23}F_3N_4O_3$: C, 63.77; H, 4.56; N, 11.02. Found: C, 63.89; H, 4.62; N, 10.95.

4.4.12. 2-Methoxycarbonylacridine ***42***. Yellowish crystals, yield 76% mp 82–83 °C. IR (KBr): ν_{max}=1732 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=4.00 (3H, s, OCH_3), 7.57 (1H, ddd, J=8.1, 7.2, 1.5 Hz, ArH), 7.85 (1H, ddd, J=8.4, 7.2, 1.5 Hz, ArH), 8.04 (1H, dd, J=8,4, 0.6 Hz, C_3–H), 8.27–8.32 (3H, m, ArH) 8.79 (1H, d, J=0.6 Hz, C_1–H), 8.92 (1H, s, C_9–H) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=52.6, 125.3, 126.4, 126.8, 127.4, 128.5, 128.9, 129.2, 129.5, 131.9, 132.2, 138.8, 149.4, 166.5, 169.8 ppm. Anal. Calcd for $C_{15}H_{11}NO_2$: C, 75.94; H, 4.67; N, 5.90. Found: C, 76.00; H, 4.65; N, 6.00.

4.4.13. 2-Methoxycarbonyl-3-phenylacridine ***43***. Yellow crystals, yield 90%, mp 156–157 °C (from MeOH). IR (KBr): ν_{max} 1724 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=3.94 (3H, s, OCH_3); 7.37 (1H, t, J=7.5 Hz, ArH), 7.47–7.58 (3H, m, ArH), 7.70 (1H, s, C(9)–H), 7.72–7.78 (3H, m, ArH), 7.82 (1H, d, J=8.7 Hz, ArH), 8.00 (1H, s, C(1)–H), 8.12 (1H, d, J=8.7 Hz, ArH), 8.16 (1H, s, C(4)–H). ^{13}C NMR (75 Hz, $CDCl_3$): δ=52.9, 124.5, 126.0, 126.7, 127.3, 127.7, 127.8, 128.0, 128.3, 128.7, 129.6, 129.7, 129.8, 130.2, 130.8, 135.8, 137.4, 149.0, 149.2, 163.7 ppm. Anal. Calcd for $C_{21}H_{15}NO_2$: C, 80.49; H, 4.82; N, 4.47. Found: C, 80.54; H, 4.92; N, 4.41.

4.4.14. 2-Methoxycarbonyl-7-methoxy-3-phenylacridine ***44***. Brownish crystals, yield 75% mp 122–123 °C. IR (KBr): ν_{max}=1726 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=3.75 (3H, s, OCH_3), 4.03 (3H, s, OCH_3), 7.23 (1H, d, J=2.7 Hz, C_8–H), 7.43–7.50 (5H, m, ArH), 7.57 (1H, dd, J=9.4, 2.7 Hz, ArH), 8.23 (1H, d, J=9.4 Hz, ArH), 8.29 (1H, s, C_1–H), 8.54 (1H, s, C_9–H), 8.77 (1H, s, C_4–H) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=52.2, 56.6, 103.2, 124.7, 127.3, 127.6, 127.6, 128.2, 128.3, 129.7, 129.9, 130.0, 131.1, 135.6, 140.5, 142.1, 146.4, 146.6, 157.5, 168.6 ppm. Anal. Calcd for $C_{22}H_{17}NO_3$: C, 76.95; H, 4.99; N, 4.08. Found: C, 77.00; H, 5.04; N, 3.99.

4.4.15. 7-Ethoxy-2-methoxycarbonyl-3-phenylacridine ***45***. Brownish crystals, yield 51% mp 120–121 °C. IR (KBr): ν_{max}=1724 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=1.53 (3H, t, J=6.9 Hz, OCH_2CH_3), 3.77 (3H, s, OCH_3), 4.19 (3H, q, J=6.9 Hz, OCH_2CH_3), 7.13 (1H, d, J=2.7 Hz, C_8–H), 7.41–7.52 (6H, m, ArH), 8.12 (1H, d, J=9.6 Hz, ArH), 8.21 (1H, s, C_1–H), 8.48 (1H, s, C_9–H), 8.64 (1H, s, C_4–H) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=14.9, 52.8, 64.2, 104.0, 125.0, 127.3, 128.2, 128.4, 128.6, 129.9, 130.8, 130.9, 131.4, 134.9, 141.0, 141.7, 147.4, 147.7, 156.9, 168.9, 170.0 ppm. Anal. Calcd for $C_{23}H_{19}NO_3$: C, 77.29; H, 5.36; N, 3.92. Found: C, 77.33; H, 5.19; N, 3.95.

4.4.16. 3-Methoxycarbonyl-2-phenyl-9H-carbazole ***46***. Yellowish crystals, yield 80% mp 165–167 °C. IR (KBr): ν_{max}=3388 (NH), 1732 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=3.69 (3H, s, OCH_3), 7.31–7.46 (8H, m, ArH), 8.11 (1H, d, J=7.8 Hz, ArH), 8.39 (1H, br s, NH), 8.67 (1H, s, C_4–H) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=51.8, 110.9, 112.6, 120.3, 120.6, 121.9, 122.0, 123.0, 123.4, 126.5, 126.9, 127.8, 128.6, 140.2, 141.0, 141.2, 142.5, 169.3 ppm. Anal. Calcd for $C_{20}H_{15}NO_2$: C, 79.72; H, 5.02; N, 4.65. Found: C, 79.77; H, 4.95; N, 4.58. Data for compound **46** are in agreement with published previosly.[23]

4.4.17. 2-(4-Methylphenyl)-3-methoxycarbonyl-9H-carbazole ***47***. Yellowish crystals, yield 62% mp 183–185 °C (from octane). IR (KBr): ν_{max}=3395 (NH), 1730 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=2.43 (3H, s, CH_3), 3.80 (3H, s, OCH_3), 7.21–7.24 (2H, m, ArH), 7.28–7.34 (4H, m, ArH), 7.46–7.49 (2H, m, ArH), 8.14 (1H, dt, J=7.8, 0.9 Hz, ArH), 8.43 (1H, br s, NH), 8.68 (1H, d, J=0.6 Hz, C_4–H) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=21.5, 52.1, 111.2, 112.9, 120.5, 120.9, 122.1, 122.2, 123.4, 123.6, 126.7, 128.7, 128.9, 136.8, 139.8, 140.5,

141.4, 141.6, 170.1 ppm. Anal. Calcd for $C_{21}H_{17}NO_2$: C, 79.98; H, 5.43; N, 4.44. Found: C, 80.17; H, 5.55; N, 4.51.

4.4.18. 2-(4-Ethylphenyl)-3-methoxycarbonyl-9H-carbazole ***48***. Yellowish crystals, yield 79% mp 154–156 °C (from octane). IR (KBr): ν_{max}=3308 (NH), 1703 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=1.29 (3H, t, J=7.8 Hz, CH_2CH_3), 2.70 (2H, q, J=7.8 Hz, CH_2CH_3), 3.77 (3H, s, OCH_3), 7.18 (2H, d, J=8.1 Hz, ArH), 7.24–7.39 (1H, m, ArH), 7.44–7.50 (6H, m, ArH), 8.14 (1H, d, J=7.5 Hz, ArH), 8.49 (1H, br s, NH), 8.69 (1H, s, C_4–H) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=15.7, 28.8, 52.2, 111.3, 113.0, 120.4, 120.8, 122.0, 122.1, 123.3, 123.6, 126.7, 127.7, 128.8, 139.9, 140.5, 141.5, 143.1, 169.9 ppm. Anal. Calcd for $C_{22}H_{19}NO_2$: C, 80.22; H, 5.81; N, 4.25. Found: C, 80.55; H, 6.00; N, 4.38.

4.4.19. Methyl dibenzofuran-2-carboxylate ***49***. Yellowish crystals, yield 79%, mp 75–77 °C. IR (KBr): ν_{max}=1715 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ=3.97 (3H, s, OCH_3), 7.38 (1H, td, J=7.5, 0.9 Hz, ArH) 7.49 (1H, td, J=7.5, 1.5 Hz, ArH), 7.60–7.56 (2H, m, ArH), 7.99 (1H, dd, J=7.8, 0.9 Hz ArH), 8.17 (1H, dd, J=8.7, 1.8 Hz, ArH), 8.68 (1H, d, J=1.5 Hz, ArH) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=52.4, 111.7, 112.1, 121.2, 123.1, 123.5, 123.9, 124.6, 125.2, 128.1, 129.1, 157.0, 159.1, 167.2 ppm. Anal. Calcd for $C_{14}H_{10}O_3$: C, 74.33; H, 4.46. Found: C, 74.48; H, 4.42. Data for compound **49** are in agreement with published previosly.[24]

4.4.20. 2-Methoxycarbonyl-3-phenyldibenzofuran ***50***. Yellowish crystals, yield 66% mp 121–123 °C. IR (KBr): ν_{max}=1732 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=3.71 (3H, s, OCH_3), 7.41–7.49 (5H, m, ArH), 7.58 (1H, s, ArH), 7.63–7.72 (1H, m, ArH), 7.72–7.79 (2H, m, ArH), 8.02–8.05 (1H, m, ArH), 8.52 (1H, s, ArH) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=52.3, 112.2, 113.9, 121.2, 123.4, 123.6, 127.6, 128.1, 128.4, 128.6, 128.7, 131.8, 132.5, 141.8, 157.2, 157.8, 169.2 ppm. Anal. Calcd for $C_{20}H_{14}O_3$: C, 79.46; H, 4.76. Found: C, 79.60; H, 4.74.

4.4.21. 5-Methoxycarbonyl-6-phenylbenzo[b]thiophene ***51***. Yellow oil, yield 60%. IR (KBr): ν_{max}=1728 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=3.66 (3H, s, OCH_3), 7.35–7.42 (6H, m, ArH, and C_3–H), 7.51 (1H, d, J=5.4 Hz, C_2–H), 7.86 (1H, s, ArH), 8.34 (1H, s, ArH) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=51.9, 123.9, 124.3, 125.5, 127.1, 127.6, 127.9, 128.0, 128.5, 138.2, 138.3, 141.4, 142.6, 169.1 ppm. Anal. Calcd for $C_{16}H_{12}O_2S$: C − 71.62, H − 4.51. Found: C − 71.77, H − 4.67.

4.4.22. 6-(4-Ethylphenyl)-5-methoxycarbonylbenzo[b]thiophene ***52***. Yellow oil, yield 64%. IR (KBr): ν_{max}=1727 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=1.34 (3H, t, J=7.8 Hz, CH_3), 2.76 (2H, q, J=7.8 Hz, CH_2), 3.74 (3H, s, OCH_3), 7.29 (2H, d, J=8.4 Hz, ArH), 7.34 (2H, d, J=8.4 Hz, ArH), 7.44 (1H, dd, J=5.4, 0.9 Hz, C_3–H), 7.54 (1H, d, J=5.4, C_2–H), 7.90 (1H, d, J=0.9 Hz, C_4–H), 8.36 (1H, s, C_7–H) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=15.7, 28.9, 52.3, 124.3, 124.6, 125.8, 127.9, 128.1, 128.8, 131.9, 138.3, 138.6, 138.9, 142.9, 143.4, 169.6 ppm. Anal. Calcd for $C_{18}H_{16}O_2S$: C, 72.94; H, 5.44. Found: C, 73.00; H, 5.49.

4.4.23. 5-Methoxycarbonylbenzo[b]thiophene ***53***. Colorless solid, yield 78%, mp 104–105 °C. IR (KBr): ν_{max}=1706 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=3.96 (3H, s, OCH_3), 7.41 (1H, d, J=5.4 Hz, C_3–H), 7.51 (1H, d, J=5.4, C_2–H), 7.92 (1H, d, J=8.5 Hz, C_7–H), 8.00 (1H, dd, J=8.5, 1.5 Hz, C_6–H), 8.53 (1H, d, J=1.5 Hz, C_4–H) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=52.2, 122.3, 124.4, 124.6, 125.5, 126.4, 127.6, 132.3, 144.1, 167.4 ppm. Anal. Calcd for $C_{10}H_8O_2S$: C, 62.48; H, 4.19. Found: C, 62.55; H, 4.22.

4.4.24. 6-Butyl-5-methoxycarbonylbenzo[b]thiophene ***54***. Yellow oil, yield 81%. IR (KBr): ν_{max}=1720 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=0.95 (3H, t, J=7.5 Hz, $CH_2CH_2CH_2CH_3$), 1.38–1.47 (2H, m, $CH_2CH_2CH_2CH_3$), 1.57–1.67 (2H, m, $CH_2CH_2CH_2CH_3$), 3.07 (2H, t, J=7.8 Hz, $CH_2CH_2CH_2CH_3$), 3.93 (3H, s, OCH_3), 7.31 (1H, d, J=5.4 Hz, C_3–H), 7.40 (1H, d, J=5.4, C_2–H), 7.38 (1H, s, C_7–H), 8.37 (1H, s, C_4–H) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=13.9, 22.7, 34.1, 34.4, 51.9, 123.9, 124.0, 126.2, 126.3, 126.6, 137.3, 139.9, 143.3, 168.3 ppm. Anal. Calcd for $C_{14}H_{16}O_2S$: C, 67.71; H, 6.49. Found: C, 67.68; H, 6.39.

4.4.25. 2-Methoxycarbonyl-6,7-dimethoxynaphthalene ***55***. White crystals, yield 79% (from compound **24**), 90% (from compound **25**), mp 95–96 °C. IR (KBr): ν_{max}=1728 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=3.99 (3H, s, OCH_3), 4.04 (3H, s, OCH_3), 4.05 (3H, s, OCH_3), 7.17 (1H, s, ArH), 7.23 (1H, s, ArH), 7.73 (1H, d, J=8.7 Hz, ArH), 7.96 (1H, dd, J=8.7, 1.5 Hz, ArH), 7.96 (1H, d, J=1.5 Hz, ArH) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=52.3, 52.9, 56.2, 106.3, 107.6, 116.2, 124.2, 126.6, 128.5, 129.5, 132.2, 150.2, 151.6, 170.0 ppm. Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.19; H, 5.74.

4.4.26. 2-Methoxycarbonyl-6,7-dimethoxy-3-phenylnaphthalene ***56***. White crystals, yield 88% mp 90–91 °C. IR (KBr): ν_{max}=1724 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=3.71 (3H, s, OCH_3), 4.04 (3H, s, OCH_3), 4.06 (3H, s, OCH_3), 7.16 (1H, s, ArH), 7.23 (1H, s, ArH), 7.42–7.44 (5H, m, ArH), 7.68(1H, s, ArH), 8.30 (1H, s, ArH) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=51.9, 55.9 ($2OCH_3$), 105.9, 106.6, 126.8, 126.9, 127.3, 127.8, 128.2, 128.5, 129.4, 130.7, 137.5, 141.8, 150.1, 151.4, 169.0 ppm. Anal. Calcd for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 74.66; H, 5.51.

4.4.27. 6-Methoxycarbonylnaphtho[2,3-d]-1,3-dioxole ***57***. White crystals, yield 98%, mp 118–120 °C. IR (KBr): ν_{max}=1709 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=3.95 (3H, s, OCH_3), 6.07 (2H, s, OCH_2O), 7.13 (1H, s, ArH), 7.19 (1H, s, ArH), 7.67 (1H, d, J=8.7 Hz, ArH), 7.90 (1H, dd, J=8.7, 1.8 Hz, ArH), 8.39 (1H, d, J=1.8 Hz, ArH) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=52.1, 101.4, 103.8, 104.9, 124.1, 127.0, 128.4, 128.6, 129.7, 132.3, 148.2, 149.5, 167.4 ppm. Anal. Calcd for $C_{13}H_{10}O_4$: C, 67.82; H, 4.38. Found: C, 68.00; H, 4.39.

4.4.28. 6-Methoxycarbonyl-7-phenylnaphtho[2,3-d]-1,3-dioxole ***58***. White crystals, yield 81%, mp 99–100 °C. IR (KBr): ν_{max}=1720 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=3.71 (3H, s, OCH_3), 6.12 (2H, s, OCH_2O), 7.15 (1H, s, ArH), 7.22 (1H, s, ArH), 7.41–7.43 (5H, m, ArH), 7.66 (1H, s, ArH), 8.25 (1H, s, ArH) ppm. ^{13}C NMR (75 Hz, $CDCl_3$): δ=52.2, 101.7, 104.0, 104.6, 127.2, 127.5, 128.2, 128.8, 128.9, 129.2, 129.3, 130.2, 132.4, 141.9, 148.6, 149.9, 169.3 ppm. Anal. Calcd for $C_{19}H_{14}O_4$: C, 74.50; H, 4.61. Found: C, 74.55; H, 4.66.

4.4.29. Methyl 4-phenylbenzoate ***59***. White crystals, yield 70%, mp 117–119 °C. IR (KBr): ν_{max}=1724 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=3.95 (3H, s, OCH_3), 7.40–7.45 (1H, m, ArH), 7.45–7.50 (2H, m, ArH), 7.60–7.70 (4H, m, ArH), 8.10–8.15 (2H, m, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ=52.6, 127.5, 127.7, 128.6, 129.3, 129.4, 130.5, 140.4, 146.0, 167.4 ppm. Anal. Calcd for $C_{12}H_{10}O_3$: C, 79.22; H, 5.70. Found: C, 79.34; H, 5.58. Data for compound **59** are in agreement with published previosly.[25]

4.4.30. Methyl 2,4-diphenylbenzoate ***60***. White crystals, yield 65%, mp 76 °C. IR (KBr): ν_{max}=1725 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=3.68 (3H, s, OCH_3), 7.35–7.46 (8H, m, ArH); 7.60–7.65 (3H, m, ArH); 7.98 (1H, dd, J=8.0, 1.2 Hz ArH).ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ=52.7, 124.4, 125.6, 127.5, 127.7, 128.0, 128.1, 128.6, 129.3, 129.4, 130.0, 130.5, 134.0, 140.4, 146.0, 167.8 ppm. Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.44; H, 5.68. Data for compound **50** are in agreement with published previosly.[26]

4.4.31. Methyl 1-hydroxy-2-naphthoate ***62***. Colorless solid, yield 55%, mp 77–79 °C. IR (KBr): ν_{max}=3299 (OH), 1660 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=3.90 (3H, s, OCH_3), 7.18 (1H, d, J=8.96 Hz, ArH), 7.40–7.53 (2H, m, ArH), 7.66 (1H, d, J=8.67 Hz, ArH), 8.32 (1H,

d, J=8.26 Hz, ArH), 11.90 (1H, s, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=52.98, 119.3, 124.6, 124.9, 125.5, 126.5, 128.1, 130.1, 137.9, 161.6 ppm. Anal. Calcd for $C_{12}H_{10}O_3$: C, 71.28; H, 4.98. Found: C, 71.49; H, 5.05. Data for compound **52** are in agreement with published previosly.[27]

4.4.32. Methyl 1-hydroxy-3-phenyl-2-naphthoate ***64***. Colorless solid, yield 39%, mp 84–85 °C. IR (KBr): ν_{max}=3284 (OH), 1668 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.99 (3H, s, OCH_3), 7.19 (1H, td, J=7.6, 1.8 Hz, ArH), 7.40–7.46 (3H, m, ArH), 7.51–7.56 (2H, m, ArH), 7.79 (1H, d, J=8.1 Hz, ArH), 7.83 (1H, dd, J=7.8, 1.5 Hz, ArH), 7.97 (1H, d, J=8.1 Hz, ArH), 8.02 (1H, dd, J=7.9, 1.2 Hz, ArH), 10.16 (1H, s, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=52.1, 122.9, 123.1, 124.4, 127.9, 128.3, 128.9, 130.3, 130.9, 131.7, 132.6, 133.9, 135.1, 138.8, 141.3, 166.9 ppm. Anal. Calcd for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07. Found: C, 77.79; H, 5.00. Data for compound **64** are in agreement with published previosly.[10]

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2010.11.073.

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