New synthesis of substituted 6-methylbenzo[*b*]furo-, -thieno-, and -seleno[2,3-*c*]quinolines, and heterocyclic analogues

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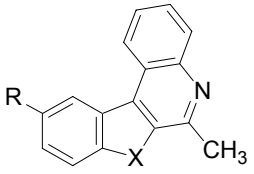
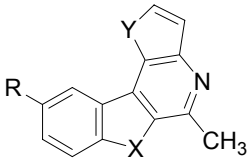
Abstract
Substituted 6-methylbenzo[*b*]furo, -thieno-, and -seleno[2,3-*c*]quinolines were synthesised either by thermal electrocyclisation of the 2-ethanonoximes of 3-phenyl- and 3-hetaryl-substituted benzo[*b*]furans, -thiophenes, and selenophene, or by treatment of the corresponding *O*-2,4-dinitrophenyl oximes with sodium hydride.

Keywords: Coupling, triflates, benzo[*b*]hetarylquinolines, electrocyclisation, oximes

Introduction

We present here the synthesis of 6-methylbenzo[*b*]furo-, thieno- and seleno[2,3-*c*]quinolines **1** and their analogues derived by replacing the benzene ring of the quinoline moiety either by thiophene **2** or furan **3**.





1a (R = Br, X = O)
1b (R = Cl, X = O)
1c (R = H, X = S)
1d (R = H, X = Se)

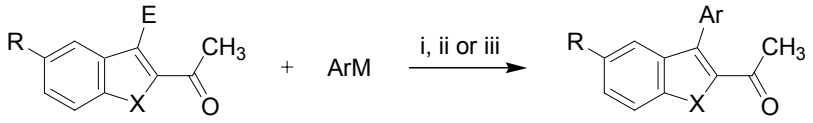
2a (R = H, X = Y = S)
2b (R = H, X = O, Y = S)
2c (R = SCH_3, X = O, Y = S)
3 (R = H, X = S, Y = O)

6-Methylbenzo[*b*]furo[2,3-*c*]quinoline **1** has previously been obtained from 2-amino-2'-hydroxybenzophenone.[1] However, this method can not lead to 6-methylbenzo[*b*]thieno- and seleno[2,3-*c*]quinolines **1** (X = S or Se) or to the heterocyclic analogues **2** and **3**. Hence, we have

developed a novel and general method for the preparation of compounds **1, 2** and **3** starting from readily available 2-acetyl-3-bromo or 2-acetyl-3-(trifluoromethanesulfonyloxy)benzo[*b*]furan, -benzo[*b*]thiophene and -benzo[*b*]selenophene.

Results and Discussion

A key step of this strategy is the preparation of 3-hetaryl-substituted 2-acetylbenzo[*b*]furan,-thiophene and -selenophene derivatives **8** by palladium-catalysed cross-coupling between 3-bromo-2-acetylbenzo[*b*]thiophene **4a**, -selenophene **4b** or diversely substituted 3-trifluoromethanesulfonyloxy)benzo[*b*]furans **5a–c**, -thiophene **5d** and various organostannanes **6a–c** or organoboronic acids **7a–c**. Compounds **4a–b** were obtained from 3-oxobenzo[*b*]thiophene or -selenophene, and the 3-trifluoromethanesulfonyloxy derivatives **5a–d** were prepared from the corresponding hydroxy derivatives as described earlier.[2,6]



4, **5** **6**, **7** **8**

Scheme 1. (i) $ArB(OH)_2$, 2N Na_2CO_3, $Pd(PPh_3)_4$, DME (for E = Br). (ii) $ArB(OH)_2$, CuI, 2N Na_2CO_3, $Pd(PPh_3)_4$, toluene (E = OTf). (iii) $ArSnBu_3$, $CuBr_2$, $Pd(PPh_3)_4$, dioxane (for E = Br or OTf). For R, X, and Ar see Table 1.

Table 1. Palladium cross-coupling reactions

Starting compound	X	R	E	ArM*	Product	Yield [%]
5a	O	Br	OTf	**6a**	**8a**	52
5a	O	Br	OTf	**7a**	**8a**	47
5b	O	Cl	OTf	**6a**	**8b**	87
5b	O	Cl	OTf	**7a**	**8b**	78
5b	O	H	OTf	**6b**	**8c**	89
5b	O	H	OTf	**7b**	**8c**	71
5c	O	SCH_3	OTf	**6b**	**8d**	94
4a	S	H	Br	**6a**	**8e**	82
4a	S	H	Br	**7a**	**8e**	76
5d	S	H	OTf	**7a**	**8e**	69
4a	S	H	Br	**6c**	**8f**	82
5d	S	H	OTf	**6c**	**8f**	77
5d	S	H	OTf	**6b**	**8g**	66

Table 1. Continued

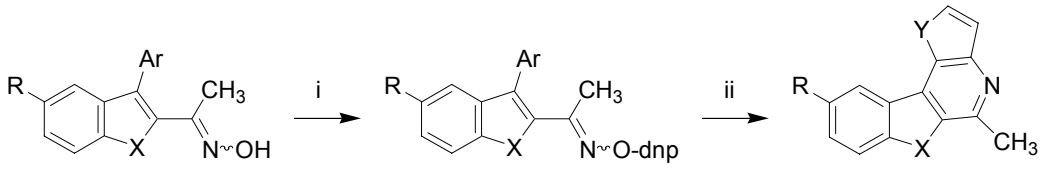
4b	Se	H	Br	**6a**	**8h**	87
4b	Se	H	Br	**7a**	**8h**	94

* **6a** = $PhSnBu_3$, **6b** = 2-thienyl $SnBu_3$, **6c** = 2-furyl$SnBu_3$; **7a** = $PhB(OH)_2$, **7b** = 2-thienyl $B(OH)_2$, **7c** = 2-furyl$B(OH)_2$

Coupling between the substituted 2-acetyl-3-bromo or 2-acetyl-3-trifluoromethane-sulfonyloxy)benzo[*b*]furans, -thiophenes and -selenophene **4** and **5**, respectively, and boronic acids **7** using a modification of Suzuki's procedure[3b,c] (Scheme 1) afforded the biaryl derivatives **8a–h** in moderate to good yields (Table 1). Similar yields of coupling products **8** were obtained by applying Stille's conditions using organostannanes **6**. The Stille reaction was carried out in refluxing dioxane in the presence of Pd^0 and $CuBr_2$ as co-catalysts[4] (Scheme 1, Table 1).

The ketoximes **9a–h** were prepared in almost quantitative yields by refluxing the corresponding ketones **8a–h** in ethanol with hydroxylamine hydrochloride and sodium acetate.

Cyclisation of oximes **9** turned out to be the critical step in the synthesis of the tetracyclic compounds **1, 2 and 3**. Thermal electrocyclisation of oximes **9** in diphenyl ether at 190 °C afforded the 6-methylbenzo[*b*]furo-, -thieno- or -seleno[2,3-*c*]quinolines **1** and their analogues **2** and **3** in yields lower than 20%.



9 **10** **1**, **2**, **3**

Scheme 2. (i) NaH 60%, THF, 1-chloro-2,4-dinitrobenzene (dnp = 2,4-$O_2NC_6H_3$). (ii) NaH 60%, dioxane. For R, X, and Ar see Table 2.

In order to improve the yields, the cyclisation was accomplished by activating oximes **9** as *O*-2,4-dinitrophenyl derivatives as it has been shown by Narasaka et al.[5] The activated compounds **10a-h**, prepared by reacting the sodium salt of the oximes **9** with 1-chloro-2,4-dinitrobenzene, were cyclised using sodium hydride in dioxane (Table 2, Scheme 2). When compound **10b** (R = Cl) was subjected to these conditions, cyclization occurred already at room temperature. Longer reaction times were required to cyclise compounds **10** which are substituted by a furan or a thiophene ring in position 3 (Table 2).

Table 2. Cyclisation of *O*-2, 4-dinitrophenyloximes **10**

Product	R	X	Ar	Y	Reaction time (h)	Yield (%)
1a	Br	O	phenyl	CH=CH	4	96
1b	Cl	O	phenyl	CH=CH	3 at r.t.	97
1c	H	Se	phenyl	CH=CH	6	84
1d	H	S	phenyl	CH=CH	4	64
2a	H	S	thienyl	S	22	56
2b	H	O	thienyl	S	24	89
2c	SCH_3	O	thienyl	S	25	63
3	H	S	furyl	O	30	82

Experimental Section

General Procedures. Melting points were determined on a Stuart Scientific melting point apparatus MP3. ^{1}H NMR spectra were recorded on an AC Bruker 250 MHz instrument. Infrared spectra (IR) were measured on a Perkin-Elmer 881 spectrometer. Compounds **4a–b** were prepared as described.[6] CH_3CN was distilled over potassium carbonate; DME was distilled over lithium aluminium hydride. Silica gel (chromagel 70–200 μm) was used for column chromatography.

General procedures for the Suzuki cross-coupling reactions

Procedure 1. Bromo derivatives **4a**–**b** (1 mmol) were dissolved in DME (50 mL) and the resultant solution was purged with nitrogen. $Pd(PPh_3)_4$ (1.1 mg, 10^{-3} mmol, 3 mol%) was added; the mixture was stirred for 15 minutes, treated with 2N aqueous sodium carbonate (2 mL) and the solution became cloudy. The boronic acids[8] **7a**–**c** (1.1 mmol.) were added as a solid. The solution was heated under reflux until **4a**–**b** was consumed (monitored by TLC). The solvent was removed in vacuum, and the residue was partitioned between diethyl ether (20mL) and water(10mL). The organic layer was separated and washed with brine, dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by column chromatography using CH_2Cl_2 as eluent to give **8e**–**h**.

Procedure 2. In an argon atmosphere, a solution of triflates **5a**–**d** (1 mmol.), boronic acid **7a**–**c** (3 mmol.), copper(I) iodide (209 mg, 1.1 mmol.), 2 N sodium carbonate (742 mg, 7 mmol.) and $Pd(PPh_3)_4$ (34 mg, 3.10^{-3} mmol, 4 mol%) in dry toluene (10 mL) was heated under reflux until **5a**–**d** has disappeared (TLC). The reaction mixture was then cooled to room temperature, and water and ethyl acetate were added. The two layers were partitioned, and the organic phase was washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography using CH_2Cl_2 as eluent to give **8**.

General procedure for the Stille cross coupling reactions

A solution of stannane **6a–c** (1.04 mmol), bromo or triflate derivative **4a,b** or **5a-d** (1 mmol), respectively, LiCl (105 mg, 3 mmol) and $Pd(PPh_3)_4$ (34 mg, 3.10^{-3} mmol, 4 mol%) in dioxane (4 mL) were refluxed in an argon atmosphere until disappearance of the triflate or the bromide (TLC). The reaction mixture was then cooled to room temperature, and water (40 mL) and ethyl acetate (25 mL) were added. The two layers were partitioned, the organic phase was separated, washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography using CH_2Cl_2 as eluent to give **8**.

1-(5-Bromo-3-phenylbenzofuran-2-yl)ethanone (8a). Colorless crystals, mp 99 °C. IR (KBr): 1686 (CO) cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.49 (s, 3H, CH_3) 7.48 (d, *J* = 7.65 Hz, 1H, ArH), 7.52 (m, 5H, ArH), 7.60 (dd, *J* = 1.67, 8.67 Hz, 1H, ArH), 7.70 (d, *J* = 1.68 Hz, 1H, ArH). Anal. Calc. for $C_{16}H_{10}BrO_2$ (315.16): C, 60.97; H, 3.52. Found: C, 60.91, H, 3.45.

1-(5-Chloro-3-phenylbenzofuran-2-yl)ethanone (8b). Colorless crystals, mp 87 °C. IR (KBr):1679 (CO) cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.49 (s, 3H, CH_3), 7.48 (m, 1H, ArH), 7.57 (m, 7H, ArH). Anal. Calc. for $C_{16}H_{10}ClO_2$ (270.70): C, 70.98; H, 3.69. Found: C, 71.08; H, 3.76.

1-[(3-Thiophen-2-yl)benzofuran-2-yl]ethanone (8c). Colorless crystals, mp 82 °C. IR (KBr): 1673 (CO) cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.62 (s, 3H, CH_3), 7.21 (dd, *J* = 2.8, 4.2 Hz, 1H, ArH), 7.36 (m, 1H, ArH), 7.55 (m, 3H, ArH), 7.72 (d, *J* = 2.8 Hz 1H, ArH), 7.93 (d, *J* = 7.98 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$): δ 189.7 (CO), 153.9, 146.9, 130.9, 127.9, 120.6 (C_q), 130.0, 128.4, 127.2, 124.0, 123.0, 112.2 (CH), 28.2 (CH_3). Anal. Calc. for $C_{14}H_{10}O_2S$ (242.22): C, 69.41; H, 4.16. Found: C, 69.54; H, 4.25.

1-[(5-Methylsulfanyl-3-thiophen-2-yl)benzofuran-2-yl]ethanone (8d). Colorless crystals, mp 61 °C. IR (KBr): 1672 (CO) cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.54 (s, 3H, CH_3), 2.6 (s, 3H, CH_3), 7.21 (dd, *J* = 3.7, 4.7 Hz, 1H, ArH), 7.49 (m, 2H, ArH), 7.53 (dd, *J* = 1.09, 4.68 Hz 1H, ArH,), 7.69 (dd, *J* = 1.1, 3.72 Hz, 1H, ArH), 7.80(d, *J* = 1.27 Hz, 1H, ArH). Anal. Calc. for $C_{15}H_{12}O_2S_2$ (288.24): C, 62.50; H, 4.19. Found: C, 62.60; H, 4.31.

1-(3-Phenylbenzo[*b*]thiophen-2-yl)ethanone (8e). Colorless crystals, mp 70 °C. IR (KBr): 1682 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.10 (s, 3H, CH_3), 7.38(m, 3H, ArH), 7.45 (d, *J* = 8.4 Hz 1H, ArH), 7.53 (m, 3H, ArH), 7.89 (d, *J* = 8.26 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$): 194.8 (CO), 142.1, 141.0; 140.9, 140.8, 134.2 (C_q), 129.7, 128.9, 128.7, 127.5, 125.7, 124.8, 122.6 (CH), 29.7 (CH_3). Anal.. Calc. for $C_{16}H_{12}OS$ (252.25): C, 76.17; H, 4.79. Found: C, 76.25; H, 4.85.

1-[3-(Furan-2-yl)benzo[*b*]thiophen-2-yl]ethanone (8f). Colorless crystals, mp 69 °C. IR (KBr): 1677 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.87 (s, 3H, CH_3), 6.66 (m, 1H), 7.48 (m, 2H, ArH), 7.68 (m, 1H, ArH) 7.89(m, 2H, ArH), 8.04(m, 1H, ArH). Anal. Calc. for $C_{14}H_{10}O_2S$ (242.22):C 69.41, H 4.16; Found: C 69.45, H 4.10

1-[3-(Thiophen-2-yl)benzo[*b*]thiophen-2-yl-ethanone (8g). Yellow oil. ^1H NMR ($CDCl_3$): δ 2.25 (s, 3H, CH_3), 7.17 (d, *J* = 3.32 Hz, 1H, ArH), 7.23 (m, 1H, ArH), 7.37 (m, 1H, ArH), 7.48 (m, 1H, ArH), 7.57 (d, *J* = 5.80 Hz, 1H, ArH), 7.60 (d, *J* = 8.12 Hz, 1H, ArH), 7.88 (d, *J* = 7.90 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$): δ 193.6 (CO), 142.9, 141.2; 140.1, 134.2, 133.6 (C_q), 129.3,

128.8, 127.6, 125.5, 125.1, 124.8, 122.6 (CH), 29.7 (CH_3). Anal. Calc. for $C_{14}H_{10}OS_2$ (226.22): C, 74.32; H, 4.45. Found: C, 74.10; H, 4.52.

1-(3-Phenylbenzoselenophen-2-yl)ethanone (8h). Colorless crystals, mp 92 °C. ^{1}H NMR ($CDCl_3$): δ 2.01 (s, 3H, CH_3), 7.35(m, 5H, ArH), 7.52 (m, 2H, ArH), 7.54 (d, *J* = 7.59 Hz, 1H, ArH), 7.93 (d, *J* = 7.86 Hz 1H, ArH); ^{13}C NMR ($CDCl_3$): δ 194.8 (CO), 145.7, 145.1; 144.2, 142.8, 136.5 (C_q), 129.5, 128.8, 128.0, 127.4, 125.7, 124.9 (CH), 29.3 (CH_3). Anal. Calc. for $C_{16}H_{12}OSe$ (299.16): C, 64.22; H, 4.04. Found: C, 64.10; H, 4.14.

Preparation of oximes 9a–g

Sodium acetate (127 mg, 1.5 mmol) and hydroxylamine hydrochloride (119 mg, 1.5 mmol) were added to a solution of ketone **8a**–**h** (1 mmol.) in ethanol (10 mL). The resulting solution was stirred under reflux for 3 h and was then poured into ice water. The resulting precipitate was filtered off, washed with water and dried in vacuum at 60 °C.

1-(5-Bromo-3-phenylbenzo[*b*]furan-2-yl)ethanone oxime (9a). Yellow solid; mp 176 °C. ^{1}H NMR ($CDCl_3$): δ 2.05 (s, 3H, CH_3), 7.45(m, 8H, ArH), 7.57 (s, 1H, OH).

1-(5-Chloro-3-phenylbenzo[*b*]furan-2-yl)ethanone oxime (9b). Beige solid; mp 168 °C. ^{1}H NMR ($CDCl_3$): δ 2.06 (s, 3H, CH_3), 7.31(dd, *J* = 2.32, 8.7 Hz 1H, ArH), 7.42 (d, *J* = 2.06 Hz 1H, ArH), 7.46(m, 6H, ArH).

1-[3-(Thiophen-2-yl)benzo[*b*]furan-2-yl]ethanone oxime (9c). Yellow solid; mp 106 °C. ^{1}H NMR ($CDCl_3$): δ 2.19 (s, 3H, CH_3), 7.17 (dd, 1H, ArH), 7.27 (m, 1H, ArH), 7.30 (d, *J* = 4.17 Hz, 1H, ArH), 7.38 (m, 1H, ArH), 7.44 (d, *J* = 4.26 Hz, 1H, ArH), 7.53 (d, *J* = 8.20 Hz, 1H, ArH), 7.66 (d, *J* = 8.06 Hz, 1H, ArH), 8.20 (s, 1H, OH).

1-[5-Methylsulfanyl-3-(thiophen-2-yl)benzo[*b*]furan-2-yl]ethanone oxime (9d). Yellow solid; mp 119 °C. ^{1}H NMR ($CDCl_3$): δ 2.17(s, 3H, CH_3), 2.5 (s, 3H, SCH_3), 7.16 (m, 1H, ArH), 7.29 (dd, *J* = 1.0, 3.6 Hz, 1H, ArH), 7.34 (dd, *J* = 1.86, 8.71 Hz, 1H, ArH), 7.44(d, *J* = 8.77 Hz, 1H, ArH), 7.49 (dd, *J* = 1.27, 5.2 Hz, 1H, ArH), 7.56 (d, *J* = 1.69 Hz 1H, ArH).

1-(3-Phenylbenzo[*b*]thiophen-2-yl)ethanone oxime (9e). Beige solid; mp 168 °C. ^{1}H NMR ($CDCl_3$): δ 1.84 (s, 3H, CH_3), 7.31(d, *J* = 7.68 Hz, 1H, ArH), 7.41 (m, 1H, ArH), 7.49 (m, 4H, ArH), 7.83 (d, *J* = 7.85 Hz, 1H, ArH), 9.09 (s, 1H, OH).

1-[3-(Furan-2-yl)benzo[*b*]thiophen-2-yl]ethanone oxime (9f). Beige solid; mp 148 °C. ^{1}H NMR ($CDCl_3$): δ 1.99 (s, 3H, CH_3), 6.59 (m, 1H, ArH), 6.62 (d, *J* = 3.86 Hz 1H, ArH), 7.39 (m, 2H, ArH), 7.60 (d, *J* = 1.70 Hz, 1H, ArH), 7.82 (dd, *J* = 1.86, 8.30 Hz, 1H, ArH), 7.85 (dd, *J* = 2.03, 8.03 Hz 1H, ArH), 8.35 (s, 1H, OH).

1-[3-(Thiophen-2-yl)benzo[*b*]thiophen-2-yl]ethanone oxime (9g). Yellow solid; mp 173 °C. ^{1}H NMR ($CDCl_3$): δ 1.95 (s, 3H, CH_3), 7.14(dd, *J* = 1.16, 3.59 Hz, 1H, ArH), 7.18(m, 1H, ArH), 7.37 (m, 2H, ArH), 7.49 (dd, *J* = 1.06 4.87 Hz, 1H, ArH), 7.67(dd, *J* = 1.90, 8.22 Hz, 1H, ArH), 7.81 (dd, *J* = 1.64, 8.69 Hz, 1H, ArH), 8.13 (s, 1H, OH).

1-(3-Phenylbenzo[*b*]selenophen-2-yl)ethanone oxime (9h). Yellow solid; mp 172 °C; ^{1}H NMR ($CDCl_3$): δ 1.73 (s, 3H, CH_3), 7.29(m, 2H, ArH), 7.36 (m, 3H, ArH), 7.46 (m, 3H, ArH), 7.67 (s, 1H, OH), 7.85 (dd, *J* = 1.20, 7.87 Hz 1H, ArH).

Preparation of *O*-(2,4-dinitrophenyl)oximes 10a–h

A solution of oxime **9a–h** (1 mmol) in dry THF (3 mL) was added dropwise to a suspension of NaH (60%, 26 mg, 1.1 mmol) in dry THF (1mL) while keeping the temperature below 5 °C. The resulting solution was stirred at room temperature for 1 hour. Then, a solution of 1-chloro-2,4-dinitrobenzene (255 mg, 1.15 mmol) in dry THF (2 mL) was added dropwise. The reaction mixture was stirred at room temperature overnight and poured into ice water. After addition of dichloromethane (20 mL) the two layers separated; the organic layer was washed with brine, dried over Na_2SO_4, and the solvent evaporated in vacuum. The crude product was purified by column chromatography (dichloromethane/cyclohexane 1:1).

1-(5-Bromo-3-phenylbenzo[*b*]furan-2-yl)ethanone *O*-(2,4-dinitrophenyl)oxime (10a). Yellow solid; mp 186 °C. ^{1}H NMR ($CDCl_3$): δ 2.56 (s, 3H, CH_3), 7.19(td, 1H, ArH), 7.53 (m, 7H, ArH), 7.62 (d, *J* = 9.38 Hz, 1H, ArH), 8.21 (dd, *J* = 2.69, 9.41 Hz, 1H, ArH), 8.86 (d, *J* = 2.54 Hz 1H, ArH).

1-(5-Chloro-3-phenylbenzo[*b*]furan-2-yl)ethanone *O*-(2,4-dinitrophenyl)oxime (10b). Yellow solid; mp 191 °C. ^{1}H NMR ($CDCl_3$): δ 2.57 (s, 3H, CH_3), 7.21(d, *J* = 9.42 Hz, 1H, ArH,), 7.42 (dd, *J* = 2.17, 8.8 Hz, 1H, ArH), 7.52(d, *J* = 2.51 Hz, 1H, ArH), 7.52 (m, 6H, ArH), 8.21 (dd, *J* = 2.72, 9.37 Hz, 1H, ArH), 8.86 (d, *J* = 2.68 Hz, 1H, ArH).

1-[(3-Thiophen-2-yl)benzo[*b*]furan-2-yl]ethanone *O*-(2,4-dinitrophenyl)oxime (10c). Yellow solid; mp 181 °C. ^{1}H NMR ($CDCl_3$): δ 2.66 (s, 3H, CH_3), 6.61(m, 1H, ArH), 7.03(d, *J* = 3.41 Hz, 1H, ArH), 7.37(m, 1H, ArH), 7.47 (d, 1H, ArH), 7.57 (d, *J* = 8.05 Hz, 1H, ArH), 7.65 (s, 1H, ArH), 7.94 (d, *J* = 8.54 Hz, 1H, ArH), 7.96 (d, *J* = 9.27 Hz, 1H, ArH), 8.46 (dd, *J* = 2.19, 9.15 Hz, 1H, ArH), 8.94 (d, *J* = 2.37 Hz 1H, ArH).

1-[5-Methylsulfanyl-3-(thiophen-2-yl)benzo[*b*]furan-2-yl]ethanone *O*-(2,4-dinitrophenyl)oxime (10d). Yellow solid; mp 184 °C. ^{1}H NMR ($CDCl_3$): δ 2.52 (s, 3H, CH_3), 2.59 (s, 3H, SCH_3), 7.27 (m, 1H, ArH), 7.43 (dd, *J* = 18.57 Hz, 1H, ArH), 7.55 (m, 3H, ArH), 7.62(d, *J* = 9.35 Hz, 1H, ArH), 8.40 (dd, *J* = 2.54, 9.38 Hz, 1H, ArH), 8.95 (d, *J* = 2.52 Hz, 1H, ArH).

1-(3-Phenylbenzo[*b*]thiophen-2-yl)ethanone *O*-(2,4-dinitrophenyl)oxime (10e). Yellow solid; mp 179 °C. ^{1}H NMR ($CDCl_3$): δ 2.22 (s, 3H, CH_3), 7.36 (m, 1H, ArH), 7.42 (d, *J* = 7.32 Hz 1H, ArH), 7.46 (m, 1H, ArH), 7.52 (m, 5H, ArH), 7.69 (d, *J* = 9.40 Hz, 1H, ArH), 7.89 (d, 1H, *J* = 8.04 Hz ArH), 8.40 (dd, *J* = 2.48, 9.32 Hz, 1H, ArH), 8.90 (d, *J* = 2.38 Hz 1H, ArH).

1-[3-(Furan-2-yl)benzo[*b*]thiophen-2-yl]ethanone *O*-(2,4-dinitrophenyl)oxime (10f). Yellow solid; mp 162 °C. ^{1}H NMR ($CDCl_3$): δ 2.30 (s, 3H, CH_3), 6.65 (m, 1H, ArH), 6.72 (d, *J* = 3.00 Hz, 1H, ArH), 7.47 (m, 2H, ArH), 7.64(d, *J* = 1.82 Hz, 1H, ArH), 7.87 (d, *J* = 8.35 Hz, 1H, ArH), 7.89 (d, *J* = 8.42 Hz, 1H, ArH), 7.99 (d, *J* = 9.44 Hz, 1H, ArH), 8.46 (dd, *J* = 2.73, 9.42 Hz, 1H, ArH), 8.92 (d, *J* = 2.56 Hz 1H, ArH).

1-[3-(Thiophen-2-yl)benzo[*b*]thiophen-2-yl]ethanone *O*-(2,4-dinitrophenyl)oxime (10g). Yellow solid; mp 176 °C. ^{1}H NMR ($CDCl_3$): δ 2.30 (s, 3H, CH_3), 7.18 (m, 2H, ArH), 7.44 (m, 2H, ArH), 7.55 (d, *J* = 5.24 Hz, 1H, ArH), 7.72 (d, *J* = 8.97 Hz, 1H, ArH), 7.80 (d, *J* = 8.819 Hz, 2H, ArH), 8.41 (dd, *J* = 2.49, 8.98 Hz, 1H, ArH), 8.92 (d, *J* = 2.48 Hz, 1H, ArH).

1-(3-Phenylbenzo[*b*]selenophen-2-yl)ethanone *O*-(2,4-dinitrophenyl)oxime (10h). Yellow solid; mp 179 °C. ^{1}H NMR ($CDCl_3$): δ 2.11 (s, 3H, CH_3), 7.26(m, 1H, ArH), 7.39 (m, 4H, ArH), 7.82 (d, *J* = 9.05 Hz, 1H, ArH), 7.92 (d, *J* = 8.03 Hz, 1H, ArH), 8.47 (dd, *J* = 2.55, 9.31 Hz, 1H, ArH), 8.90 (d, *J* = 2.56 Hz 1H, ArH).

Cyclisation of *O*-(2,4-dinitrophenyl)oximes 10a–h

A solution of *O*-(2,4-dinitrophenyl)oxime **10a–h** (1 mmol) in dioxane (1.5 mL) of was added dropwise to a suspension of NaH (60%, 240 mg, 10 mmol) in dioxane (1 mL). The reaction mixture was heated under reflux until the starting material had disappeared (TLC). The cooled reaction mixture was poured into ice water and extracted with diethyl ether. The organic layer was separated, washed with brine, dried over Na_2SO_4, and evaporated in vacuum. The crude product was purified by column chromatography (eluent: dichloromethane).

10-Bromo-6-methylbenzo[*b*]furo[2,3-*c*]quinoline (1a). Yellow solid; mp 198 °C. ^{1}H NMR ($CDCl_3$): δ 3.01 (s, 3H, CH_3), 7.65 (d, *J* = 7.76 Hz, 1H, ArH), 7.72 (m, 2H, ArH), 7.74 (dd, *J* = 1.77, 7.74 Hz, 1H, ArH), 8.24 (dd, *J* = 2.44, 8.33 Hz, 1H, ArH), 8.43 (dd, *J* = 2.67, 8.17 Hz, 1H, ArH), 8.53 (d, *J* = 1.57 Hz, 1H, ArH); ^{13}C NMR: δ 154.8, 146.8, 143.7, 138.7, 138.3, 125.6, 123.2, 116.8 (C), 131.4, 129.7, 127.8, 127.0, 125.9, 123.1, 114.2 (CH), 19.7 (CH_3). Anal. Calc. for $C_{16}H_{10}BrNO$ (312.16): C, 61.55; H, 3.23; N, 4.49. Found: C, 61.48; H, 3.19; N, 4.35.

10-Chloro-6-methylbenzo[*b*]furo[2,3-*c*]quinoline (1b). Yellow solid mp 191 °C. ^{1}H NMR ($CDCl_3$): δ 3.01 (s, 3H, CH_3), 7.59 (m, 1H, ArH), 7.70 (d, *J* = 7.72 Hz 1H, ArH), 7.74 (m, 2H, ArH), 8.21 (dd, *J* = 2.23, 8.22 Hz, 1H, ArH), 8.36 (s, 1H, ArH), 8.45 (dd, *J* = 8.19 Hz, 1H, ArH); ^{13}C NMR: δ 166.0, 154.3, 151.0, 146.8, 144.4, 129.4, 124.9, 123.2 (C), 129.8, 128.6, 127.6, 127.0, 123.0, 122.8, 113.7 (CH), 22.7 (CH_3). Anal. Calc. for $C_{16}H_{10}ClNO$ (267.70): C, 71.78; H, 3.76; N, 5.23. Found: C, 71.65; H, 3.80; N, 5.21.

6-Methylbenzo[*b*]seleno[2,3-*c*]quinoline (1c). Yellow solid; mp 134 °C. ^{1}H NMR ($CDCl_3$): δ 2.98 (s, 3H, CH_3), 7.55 (m, 1H, ArH), 7.72 (m, 3H, ArH), 8.10 (d, *J* = 7.84 Hz, 1H, ArH), 8.23 (d, *J* = 7.94 Hz, 1H, ArH), 8.93 (d, *J* = 8.07 Hz, 2H, ArH). Anal. Calc. for $C_{16}H_{11}NSe$ (296.16): C, 64.87; H, 3.74; N, 4.73. Found: C, 64.78; H, 3.82; N, 4.75.

6-Methylbenzo[*b*]thieno[2,3-*c*]quinoline (1d). Yellow solid; mp 105 °C. ^{1}H NMR ($CDCl_3$): δ 3.00 (s, 3H, CH_3), 7.66 (m, 2H, ArH), 7.74 (m, 2H, ArH), 8.06 (dd, *J* = 1.60, 7.92 Hz, 1H, ArH), 8.26 (dd, *J* = 7.80 Hz, 1H, ArH), 8.89 (m, 2H, ArH). Anal. Calc. for $C_{16}H_{11}NS$ (249.25): C, 77.09; H, 4.45; N, 5.62. Found: C, 77.20; H, 4.52; N, 5.70.

5-Methylbenzo[*b*]thieno[3,2-*d*]thieno[3,2-*b*]pyridine (2a). Yellow solid, m.p.147 °C. ^{1}H NMR ($CDCl_3$): δ 2.88(s, 3H, CH_3), 7.62 (m, 2H, ArH), 7.71 (d, *J* = 5.43 Hz, 1H), 7.75 (d, *J* = 5.44 Hz, 1H), 8.03 (dd, *J* = 3.24, 7.69 Hz 1H, H-7), 8.44 (dd, *J* = 3.14, 7.59 Hz 1H, H-10). Anal. Calc. for $C_{14}H_9NS_2$ (255.22): C, 65.88; H, 3.55; N, 5.49. Found: C, 65.82; H, 3.52; N, 5.54.

5-Methylbenzo[*b*]furo[3,2-*d*]thieno[3,2-*b*]pyridine (2b). White solid; mp 98 °C. ^{1}H NMR ($CDCl_3$): δ 2.98 (s, 3H, CH_3), 7.52 (m, 1H, ArH), 7.65 (m, 1H, ArH), 7.69 (d, *J* = 5.53 Hz, 1H, ArH), 7.74 (d, *J* = 8.56 Hz, 1H, ArH), 7.75 (d, *J* = 5.53 Hz, 1H, ArH), 8.12 (d, *J* = 7.55 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$): δ 156.4, 151.1, 142.1, 141.1, 130.1, 121.6, 120.7 (C), 129.3, 125.0,

123.6, 122.7, 112.5 (CH), 19.0 (CH_3). Anal. Calc. for $C_{14}H_9NOS$ (239.22): C, 70.28; H, 3.79; N, 5.88. Found: C, 70.50; H, 3.85; N, 5.80.

5-Methyl-9-methylsulfanylthieno[3,2-*b*]benzo[*b*]furo[3,2-*d*]pyridine (2c). Yellow solid, mp 157 °C. ^{1}H NMR ($CDCl_3$): δ 2.63 (s, 3H, CH_3), 2.94 (s, 3H, CH_3), 7.59 (dd, *J* = 1.66, 8.80Hz 1H, ArH), 7.65(d, *J* = 8.81 Hz, 1H, ArH), 7.66 (d, *J* = 5.44 Hz, 1H, ArH), 7.72 (d, *J* = 5.43 Hz 1H, ArH), 7.99 (d, *J* = 1.65 Hz, 1H, ArH). Anal. Calc. for $C_{15}H_{11}NOS_2$ (285.39): C, 63.15; H, 3.88; N, 54.91. Found: C, 63.12; H, 3.80; N, 4.82.

5-Methylbenzo[*b*]thieno[3,2-*d*]furo[3,2-*b*]pyridine (3). Yellow solid, mp 93 °C. ^{1}H NMR ($CDCl_3$): δ 2.89 (s, 3H, CH_3), 7.12 (d, *J* = 2.11 Hz, 1H, ArH), 7.61 (m, 2H, ArH), 7.91 (d, *J* = 2.09 Hz, 1H, ArH), 7.97 (dd, *J* = 1.42, 8.36 Hz, 1H, ArH), 8.65 (dd, *J* = 2.10, 9.05 Hz, 1H, ArH); ^{13}C NMR: δ 148.6, 146.1, 142.4, 1401, 132.1, 118.2, 113.0 C, 128.0, 125.7, 124.9, 122.5 (CH), 30.4 (CH_3). Anal. Calc. for $C_{14}H_9NOS$ (239.22): C, 70.28; H, 3.79; N, 5.85. Found: C, 70.40; H, 3.65; N, 5.95.

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