Tetrahedron 69 (2013) 3167–3181

Contents lists available at SciVerse ScienceDirect

Tetrahedron

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

Efficient synthesis of novel thieno[3,2-*b*]-, [2,3-*c*]- and [3,2-*c*] pyridones by Sonogashira coupling of bromothiophenes with terminal alkynes and subsequent intramolecular C–N bond-forming reaction

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ARTICLE INFO

Article history:
Received 9 December 2012
Received in revised form 15 February 2013
Accepted 20 February 2013
Available online 26 February 2013

Keywords:
Sonogashira coupling
Bromothiophenes
Terminal alkynes
Thienyl acetylenes
Thieno[3,2-*b*]-, [2,3-*c*]-, and [3,2-*c*] pyridones

ABSTRACT

The coupling of bromothiophenes with terminal alkynes using triethylamine or diisopropyl amine under Sonogashira conditions ($PdCl_2(PPh_3)_2$, CuI) followed by subsequent addition of amines or ammonium to the intermediate thienyl acetylenes represents a novel access to a wide range of thieno[3,2-*b*]-, [2,3-*c*]-, and [3,2-*c*]pyridones under basic conditions and in excellent yields.

1. Introduction

Functionalized quinolines are very attractive targets for combinatorial library synthesis due to their wide range of valuable biological activities.[1] Many natural and synthetic quinolines have occupied an important place in drug research. At the same time, a very special position among all drugs containing a quinoline core is occupied by the fluoroquinolones. The latter constitute a major class of antibacterial chemotherapeutic agents, which have a broad spectrum against Gram positive and Gram negative bacteria.[2] The five representatives depicted in Fig. 1 belong to the 200 top-selling drugs. Examples include norfloxacin **Ia**[3] and ciprofloxacin **Ib**,[4] which were the first two quinolones marketed for human use.

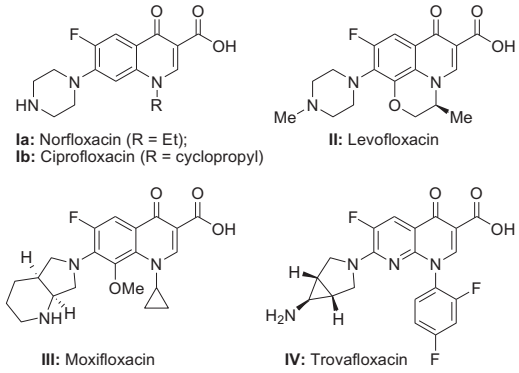

Fig. 1. Some marketing drugs containing quinolone framework.

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http://dx.doi.org/10.1016/j.tet.2013.02.069

Since 1986, more than twenty fluoroquinolones have been approved and most of them remain on the market.[2b] The biological importance of quinolones has led to a considerable amount of synthetic work in the field of this heterocyclic system[5] (Fig. 1).

Continuing our research on the efficient synthesis of drug-like heteroannulated pyridines,[6] of the six theoretically possible parent thienopyridine compounds, we sought to prepare thieno[3,2-*b*]-, [2,3-*c*]-, and [3,2-*c*]pyridines with the concept of replacing the benzene ring of the quinoline nucleus by thiophene, a known bioisostere in other fields of medicinal chemistry (Fig. 2). Earlier, synthesis of several 4-oxothieno[2,3-*b*]pyridine-5-carboxylic acids **V**, potential bioisosteres of quinolone antibacterials that exhibited good level of activity against Gram negative and Gram positive bacterial strains, has been reported.[7] Compounds **VI** have the ability to penetrate cells and selectively inhibit the surface expression of the cell adhesion molecules ICAM-1 and E-selectin in human endothelial cells,[8] while the 7-oxothieno[3,2-*b*]pyridine-6-carboxamides **VII**, a new class of non-nucleoside antivirals, possess remarkable potency versus a broad spectrum of herpesvirus DNA polymerases and excellent selectivity compared to human DNA polymerases[9] (Fig. 2).

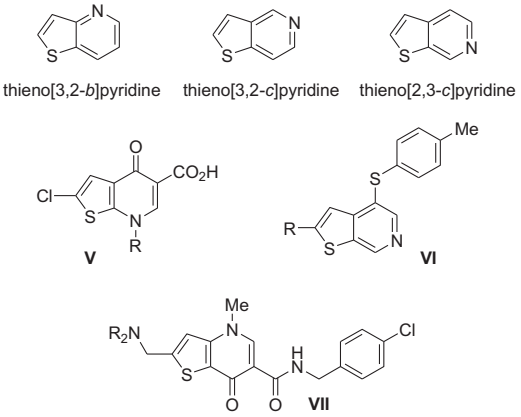
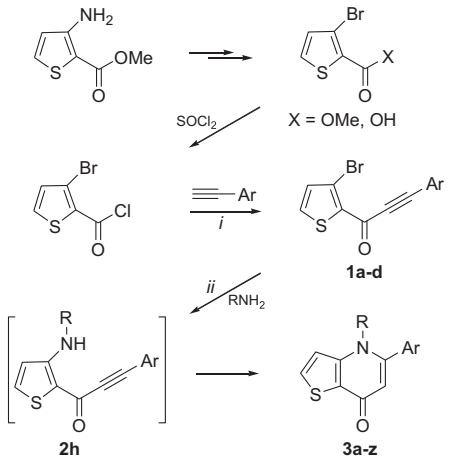


Fig. 2. Thieno[3,2-*b*]-, [3,2-*c*]-, and [2,3-*c*]pyridines and some bioactive representatives.

Given the broad utility of thienopyridines in medicinal chemistry, we were interested in developing novel approaches, commencing with bromothiophenes-based substrates, which would allow access to these interesting heterocyclic compounds. There are several different synthetic procedures leading to thienopyridines,[10] some of them use 2- and 3-aminothiophenes salts as key intermediates in the reactions with 1,3-dicarbonyls and ethoxymethylene derivatives of various active methylene compounds (Gould–Jacobs reaction).[10g–m] Though some of the known methods of preparation of thienopyridines seem to be satisfactory, new routes starting from different materials are desirable for efficient structure modifications of these molecules. In this paper we detail the successful realization of our goal with an efficient synthesis of diverse thieno[3,2-*b*]-, [2,3-*c*]-, and [3,2-*c*]pyridones by the coupling of bromothiophenes with terminal alkynes under Sonogashira conditions followed by subsequent [5+1]-cyclization of the intermediate thienyl acetylenes with a set of aromatic and aliphatic amines or ammonium.

2. Results and discussion

Based on the retrosynthetic analysis and on previous experience of Iaroshenko's group related to the development of new coupling reactions of alkynyl thiophenes[11] and alkynyl pyridines,[12] we envisaged that 1-(3-bromothiophen-2-yl)-3-arylprop-2-yn-1-ones **1** are suitable substrates for the synthesis of thieno[3,2-*b*]pyridin-7-one derivatives **3**. The requisite starting material, 3-bromothiophene-2-carbonyl chloride, was prepared by the deaminative bromination of commercially available methyl 3-aminothiophene-2-carboxylate with *tert*-butyl nitrite and $CuBr_2$ in acetonitrile,[13] followed by alkaline hydrolysis and subsequent treatment with thionyl chloride according to the described procedures (see the Experimental part). The preparation of ynones **1** was carried out by Sonogashira cross-coupling reaction[14] of 3-bromothiophene-2-carbonyl chloride with terminal aryl acetylenes using $PdCl_2(PPh_3)_2$ and CuI in the presence of triethylamine in THF to give ketones **1a**–**d** in high yields (70–77%). Then we examined the reactions of these ketones with a range of commercially available aromatic and aliphatic amines. After the optimization of the reaction conditions with regard to the type of catalyst and solvent, we have found that the use of $Pd_2(dba)_3$ (5 mol %), BINAP (10 mol %), 1.4 equiv of Cs_2CO_3 as a base, and toluene as a solvent (110 °C, 10–12 h, argon) was essential to get excellent yields (70–92%) of 4,5-disubstituted thieno[3,2-*b*]pyridones **3a**–**z**. This is a palladium-catalyzed tandem reaction consisting of a sequential double C–N bond formation to give thieno[3,2-*b*]pyridones **3** from thienyl acetylenic ketones **1** and primary amines via intermediates **2**, from which compound **2h** was isolated in 66% yield when the reaction was run for the short time (5 h) (Scheme 1).



Scheme 1. Reagents and conditions: i, $PdCl_2(PPh_3)_2$, CuI, Et_3N, THF, Ar, rt, 2 h; ii, Cs_2CO_3, $Pd_2(dba)_3$, BINAP, Ar, toluene, 110 °C, 10–12 h.

The progress of the reaction was monitored by TLC, and the results are summarized in Table 1. It is important that a wide range of aromatic and aliphatic amines can effectively participate in the reaction with acetylenic ketones **1a**–**d**, providing a variety of thieno[3,2-*b*]pyridones **3** with high purity after column chromatography. It can be observed that the process tolerates both electron-donating (alkyl, alkoxy, diethylamino) and electron-withdrawing (halogeno, nitro) substituents on the aromatic amines. The structures of all products **3** were characterized by IR, ^1H, ^{13}C NMR spectral data as well as HRMS analysis. Finally the structures of the representatives **3a** and **3m** were corroborated by X-ray single crystal analysis (Figs. 3 and 4).

Next, we have obtained a series of thieno[2,3-*c*]pyridones **6** by Sonogashira coupling of methyl 3-bromothiophene-2-carboxylate with various terminal aryl and alkyl alkynes followed by a base-mediated intramolecular C–N bond-forming reaction (Scheme 2). It was found that treatment of methyl 3-bromothiophene-2-carboxylate with the corresponding alkyne in a pressure tube under argon at 70 °C in the presence of $PdCl_2(PPh_3)_2$ (5 mol %) and CuI (3 mol %) in diisopropyl amine resulted in the formation of thienyl

Table 1
Yields of compounds **1**–**3**

1–3	Ar	R	Yield (%)
1a	Ph	—	77
1b	4-MeC_6H_4	—	73
1c	4-*n*-PrC_6H_4	—	75
1d	4-$MeOC_6H_4$	—	70
2h	Ph	4-$Et_2NC_6H_4$	66
3a	Ph	Ph	78
3b	Ph	4-MeC_6H_4	80
3c	Ph	4-EtC_6H_4	82
3d	Ph	4-$MeOC_6H_4$	78
3e	Ph	4-$EtOC_6H_4$	82
3f	Ph	2,4-$(MeO)_2C_6H_3$	70
3g	Ph	3,4,5-$(MeO)_3C_6H_2$	80
3h	Ph	4-$Et_2NC_6H_4$	80
3i	Ph	4-FC_6H_4	83
3j	Ph	3-$CF_3C_6H_4$	81
3k	Ph	3-BrC_6H_4	78
3l	Ph	4-$NO_2C_6H_4$	86
3m	Ph	4-$MeC_6H_4CH_2$	90
3n	Ph	3-$MeOC_6H_4CH_2$	92
3o	Ph	$PhCH_2CH_2$	91
3p	Ph	*c*-C_6H_{11}	90
3q	Ph	*n*-C_7H_{15}	89
3r	4-MeC_6H_4	4-$MeOC_6H_4$	82
3s	4-MeC_6H_4	4-FC_6H_4	85
3t	4-MeC_6H_4	4-ClC_6H_4	78
3u	4-*n*-PrC_6H_4	Ph	83
3v	4-*n*-PrC_6H_4	3-FC_6H_4	81
3w	4-*n*-PrC_6H_4	3,5-$Cl_2C_6H_3$	85
3x	4-$MeOC_6H_4$	4-MeC_6H_4	80
3y	4-$MeOC_6H_4$	4-EtC_6H_4	79
3z	4-$MeOC_6H_4$	4-ClC_6H_4	82

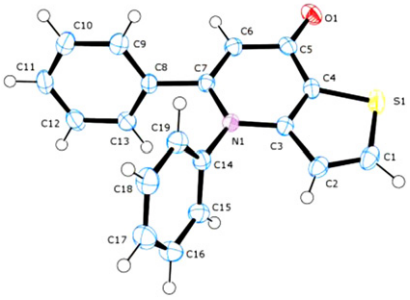


Fig. 3. Molecular structure of compound **3a**.

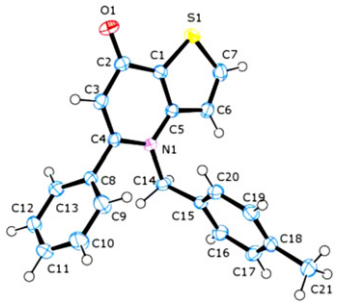
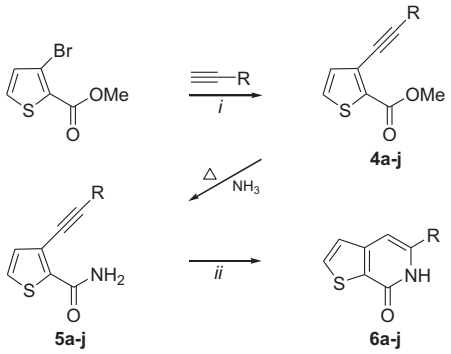


Fig. 4. Molecular structure of compound **3m**.

alkynes **4a**–**j** in good to high yields (50–75%). In most cases, the reaction was complete after 2 h and the products were purified by silica gel column chromatography. As can be seen from Table 2, this coupling reaction has virtually no limitations as regards the nature of the terminus of the alkynyl moiety. Although the chemistry of



Scheme 2. Reagents and conditions: i, $PdCl_2(PPh_3)_2$, CuI, diisopropyl amine (DIPA), Ar, 70 °C, 2 h; ii, MeONa, MeOH, reflux, 3–4 h.

Table 2
Yields of compounds **4**–**6**

4–6	R	Yield (%)		
		4	**5**	**6**
a	Ph	72	86	75
b	4-MeC_6H_4	69	88	77
c	2-MeC_6H_4	68	85	77
d	4-*n*-PrC_6H_4	73	90	72
e	4-*t*-BuC_6H_4	70	84	70
f	4-$MeOC_6H_4$	70	81	76
g	4-FC_6H_4	75	80	75
h	*n*-Pr	50	86	75
i	*n*-Bu	51	80	73
j	*n*-Am	55	81	70

thiophenes has been well documented,[15] compounds **4** are hitherto unreported. Reaction of alkynes **4a**–**j** with aqueous ammonia at heating for 10–12 h in a pressure tube produced amides **5a**–**j** in 80–90% yields. These compounds were reacted with MeONa in methanol at reflux to form thieno[2,3-*c*]pyridones **6a**–**j** in 70–77% yields by intramolecular cyclization reaction (Table 2). The structures of compounds **5c** and **6d** were confirmed by X-ray single crystal analysis (Figs. 5 and 6).

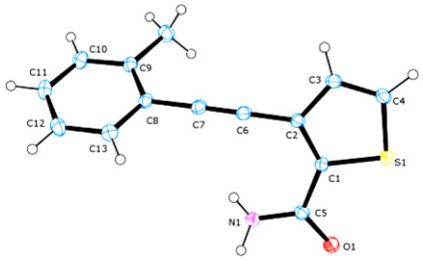


Fig. 5. Molecular structure of compound **5c**.

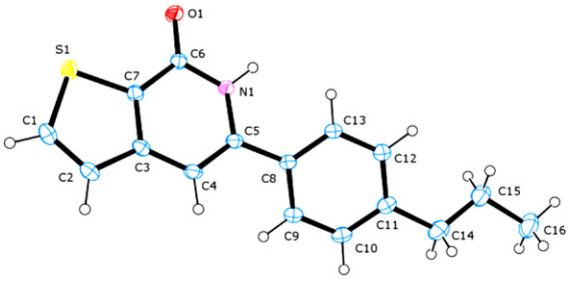
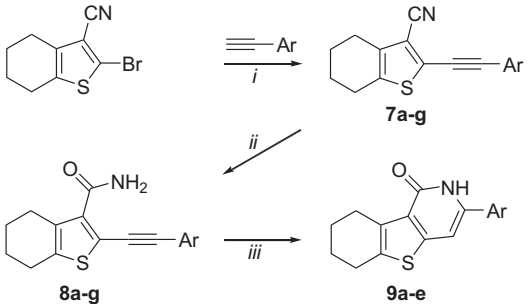


Fig. 6. Molecular structure of compound **6d**.

2-Bromo-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile, the starting material for the synthesis of thieno[3,2-*c*]pyridones **9**, was obtained by the deaminative bromination of commercially available 2-amino-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile, following the recently described method,[13] in 74% yield. The requisite thieno[3,2-*c*]pyridones **9a**–**e** can be easily prepared by the palladium/copper-catalyzed Sonogashira coupling of the corresponding aryl alkynes with 2-bromo-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile, followed by hydrolysis of the cyano group of the resultant alkynes **7a**–**g** under the action of TFA–H_2SO_4 system to amides **8a**–**g** and their intramolecular cyclization with MeONa. The introduction of substituents on the aryl group has little effect on the yields of these reactions (Scheme 3, Table 3).



Scheme 3. Reagents and conditions: i, $PdCl_2(PPh_3)_2$, CuI, diisopropyl amine (DIPA), Ar, 70 °C, 2 h; ii, TFA–H_2SO_4, 75 °C, 5 h; iii, MeONa, MeOH, reflux, 3–4 h.

Table 3
Yields of compounds **7**–**9**

7–**9**	Ar	Yield (%)		
		7	**8**	**9**
a	Ph	77	75	78
b	4-MeC_6H_4	77	77	77
c	4-*n*-PrC_6H_4	73	79	80
d	4-*t*-BuC_6H_4	73	74	79
e	4-$MeOC_6H_4$	75	77	73
f	2-MeC_6H_4	78	79	—
g	4-FC_6H_4	75	72	—

These results clearly show that the present reactions could be applicable to various types of thienyl alkynes, providing a simple and efficient route to the synthesis of a wide range of the thienopyridine derivatives, which are of interest as biologically active compounds. The structures of all the compounds were deduced from their spectral studies (IR, ^1H, ^{13}C NMR, and MS); the most of them mass spectra displayed molecular ion peaks at the appropriate *m*/*z* values.

3. Conclusion

In conclusion, we have developed an efficient synthesis libraries of thieno[3,2-*b*]-, [2,3-*c*]-, and [3,2-*c*]pyridine scaffolds on the basis of thienyl acetylenes, which were prepared by Sonogashira cross-coupling reaction. This methodology is a valuable addition to fused pyridine synthesis and represent a novel and general route to various thienopyridones, which constitute an important structural subunit of a variety of biologically active compounds.

4. Crystallographic data

Crystallographic data (excluding structure factors) for the structure **3a**, **3m**, **5c**, **6d**, reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 924461–924464 and can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk, or via www.ccdc.cam.ac.uk/data_request/cif.

5. Experimental

5.1. General

The dry solvents were purchased directly from Acros Organics as AcroSeal bottles. Other solvents were purified by distillation. All reactions were carried out under an inert atmosphere. ^1H and ^{13}C NMR spectroscopy: Bruker AV 300 and Bruker AV 400 spectrometers. References: 0.00 ppm for TMS, 7.26 ppm for $CDCl_3$ (^1H NMR) and 0.00 ppm for TMS, 77.00 ppm for $CDCl_3$ (^{13}C NMR). The DEPT method was used for determining the presence of primary, secondary, tertiary, and quaternary carbon atoms. The ^1H NMR spectra were measured with standard number of scans; ^{13}C NMR spectra were measured with standard number of scans or when necessary, with 4000 scans. In case of unclear assignment all possible hydrogen and carbon atoms were stated. ^{19}F NMR spectra were recorded on a Bruker AV 300 (282 MHz) spectrometer. The spectra were measured with standard number of scans. Mass spectrometry (MS): Finnigan MAT 95 XP (electron ionization EI, 70 eV). High-resolution MS (HRMS): Finnigan MAT 95 XP. Only the measurements with an average deviation from the theoretical mass of ±2 mDa were accounted as correct. Infrared spectroscopy (IR): Nicolet 550 FT-IR spectrometer with ATR sampling technique for solids as well as liquids. Signal characterization: w=weak, m=medium, s=strong. X-ray crystallography: STOE imaging plate diffraction systems with monochromatic Mo-Kα radiation. Elemental analysis (EA): Leco 932 C, H, N, S. UV/vis spectroscopy: Lambda 2 (Perkin–Elmer). Melting point determination (mp): Micro-Hot-Stage Galen TM III Cambridge Instruments. The melting points are not corrected. Thin layer chromatography (TLC): Merck Silica 60 F_{254} aluminum-backed plates from Macherey–Nagel. Detection with UV light at 254 nm and afterward development with vanillin–sulfuric acid solution (6 g vanillin, 2.5 ml concentrated H_2SO_4, 250 ml EtOH). Column chromatography: separation on Fluka silica gel 60 (0.063–0.200 mm, 70–320 mesh). Eluents were distilled before use. 3-Bromothiophene-2-carbonyl chloride was prepared according to the methods reported in the Ref. 16.

*5.1.1. General procedure for the synthesis of 1-(3-bromothiophen-2-yl)-3-arylprop-2-yn-1-ones (**1**).* A mixture of 3-bromothiophene-2-carbonyl chloride (0.225 g, 1.0 mmol), $PdCl_2(PPh_3)_2$ (2 mol %), and Et_3N (1.0 mmol) was stirred in anhydrous THF for 10 min under argon at room temperature. CuI (4 mol %) was added and the reaction mixture was stirred for another 10 min before aryl acetylene (1.0 mmol) was added. After 2 h at room temperature the reaction mixture was diluted with EtOAc and washed with 0.1 N HCl (2×10 ml) and saturated NH_4Cl solution (10 ml). The organic phase was separated, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography.

*5.1.2. General procedure for the synthesis of thieno[3,2-b]pyridones (**3**).* To the ynone **1** (0.5 mmol), Cs_2CO_3 (0.7 mmol), $Pd_2(dba)_3$ (5 mol %), and BINAP (10 mol %) under argon was added toluene (10 ml) followed by arylamine/alkylamine (0.6 mmol), and the reaction was stirred at 110 °C for 10–12 h. After cooling to room temperature, the reaction mixture was preabsorbed onto silica gel and purified by column chromatography.

*5.1.3. General procedure for the synthesis of esters (**4**).* A mixture of methyl 3-bromothiophene-2-carboxylate (0.221 g, 1.0 mmol), aryl/

alkyl acetylene (1.1 equiv), $PdCl_2(PPh_3)_2$ (5 mol %), CuI (3 mol %), and diisopropyl amine (DIPA) (5 ml) were added to a pressure tube under argon and then heated for 2 h at 70 °C. After cooling, water and ethyl acetate were added and the phases were separated. The aqueous phase was then extracted with ethyl acetate (3×10 ml). The combined organic layers were dried (Na_2SO_4), filtered, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography.

*5.1.4. General procedure for the synthesis of 3-(aryl/alkylethynyl) thiophene-2-carboxamides (**5**).* An ethanol solution (10 ml) of the corresponding compound **4** (0.1 g) was saturated with aqueous ammonia and heated for 10–12 h in a pressure tube at 70 °C. After completion of the reaction, solvent was removed under reduced pressure and the residue was purified with silica gel column chromatography.

*5.1.5. General procedure for the synthesis of thienopyridones (**6**).* To the methanol solution of the corresponding amide **5** (0.1 g), was added NaOMe (0.15 g) and was refluxed for 3–4 h. After completion of the reaction, methanol was removed under reduced pressure and the residue was diluted with water. The precipitate so formed was filtered, dried, and recrystallized from MeOH.

*5.1.6. General procedure for the synthesis of methyl 3-(aryl/alkylethynyl)thiophene-2-carboxylates (**4**) and 2-(arylethynyl)-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carbonitriles (**7**).* A mixture of methyl 3-bromothiophene-2-carboxylate or 2-bromo-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile (1.0 mmol), aryl/alkyl acetylene (1.1 equiv), $PdCl_2(PPh_3)_2$ (5 mol %), CuI (3 mol %), and diisopropyl amine (DIPA) (5 ml) were added to a pressure tube under argon and then heated for 2 h at 70 °C. After cooling, water and ethyl acetate were added and the phases were separated. The aqueous phase was then extracted with ethyl acetate (3×10 ml). The combined organic layers were dried (Na_2SO_4), filtered, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography.

*5.1.7. General procedure for the synthesis of 2-(arylethynyl)-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carboxamides (**8**).* A solution of the corresponding nitrile **7** (0.15 g) in 7.0 ml of TFA–H_2SO_4 (4:1, v/v) mixture was heated at reflux (75 °C). The progress of the reaction was monitored by TLC analysis. After completion of the reaction (5 h), the reaction mixture was poured into ice-cold water. The product thus precipitated out was filtered, washed with water, and dried.

*5.1.8. General procedure for the synthesis of 5-aryl/alkylthieno[2,3-c] pyridin-7(6H)-ones (**6**) and 3-aryl-6,7,8,9-tetrahydro[1]benzothieno [3,2-c]pyridin-1(2H)-ones (**9**).* To the methanol solution of the corresponding amide **5** or **8** (0.1 g), was added NaOMe (0.15 g) and was refluxed for 3–4 h. After completion of the reaction, methanol was removed under reduced pressure and the residue was diluted with water. The precipitate so formed was filtered, dried, and recrystallized from MeOH.

6. Analytical data

6.1. 1-(3-Bromothiophen-2-yl)-3-phenylprop-2-yn-1-one (1a)

Yellow solid, yield 77%, mp 81–83 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.09 (d, *J*=5.2 Hz, 1H), 7.31–7.42 (m, 3H), 7.54 (d, *J*=5.2 Hz, 1H), 7.59–7.63 (m, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=87.3, 94.0, 116.4, 119.9, 128.7, 131.0, 133.0, 133.6, 134.0, 137.9, 168.2; GC–MS (EI, 70 eV): *m*/*z* (%)=292 (M^+, ^{81}Br, 54), 290 (M^+, ^{79}Br, 52), 264 (100), 183 (3), 139 (52), 129 (64), 101 (9), 91 (7), 82 (7), 75 (17); HRMS (ESI): calcd for $C_{13}H_7{}^{79}BrOS$ 289.93955, found 289.94027 and calcd for $C_{13}H_7{}^{81}BrOS$ 291.93750, found 291.93839; IR (ATR, cm^{-1}): ν=3389 (w), 3099 (w), 2959 (w), 2794 (w), 2437 (w), 2350 (w), 2269 (w), 2192 (s), 1985 (w), 1887 (w), 1803 (w), 1651 (w), 1631 (w), 1584 (s), 1557 (w), 1531 (w), 1486 (s), 1440 (m), 1397 (s), 1347 (w), 1328 (w), 1304 (s), 1198 (s), 1095 (w), 1067 (w), 1027 (w), 966 (w), 962 (s), 918 (w), 902 (w), 877 (s).

6.2. 1-(3-Bromothiophen-2-yl)-3-*p*-tolylprop-2-yn-1-one (1b)

Yellow solid, yield 73%, mp 71–73 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.34 (s, 3H, Me), 7.09 (d, *J*=5.2 Hz, 1H), 7.15 (d, *J*=8.0 Hz, 2H), 7.53 (d, *J*=5.2 Hz, 1H), 7.51 (d, *J*=8.0 Hz, 2H); GC–MS (EI, 70 eV): *m*/*z* (%)=306 (M^+, ^{81}Br, 77), 304 (M^+, ^{79}Br, 75), 278 (100), 197 (11), 153 (19), 143 (49), 115 (8), 98 (4), 89 (8), 82 (6); HRMS (ESI): calcd for $C_{14}H_9{}^{79}BrOS$ 303.95520, found 303.95576 and calcd for $C_{14}H_9{}^{81}BrOS$ 305.95315, found 305.95370; IR (ATR, cm^{-1}): ν=3209 (w), 3105 (w), 3027 (w), 2911 (w), 2859 (w), 2291 (w), 2188 (s), 1903 (w), 1664 (w), 1619 (s), 1602 (m), 1505 (m), 1486 (s), 1454 (w), 1445 (w), 1393 (s), 1351 (s), 1304 (w), 1278 (m), 1238 (w), 1188 (m), 1174 (m), 1148 (m), 1116 (w), 1085 (w), 1010 (s), 962 (w), 945 (w), 900 (w), 879 (s), 851 (w), 809 (s).

6.3. 1-(3-Bromothiophen-2-yl)-3-(4-propylphenyl)prop-2-yn-1-one (1c)

Yellow oil, yield 75%. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.86 (t, *J*=7.4 Hz, 3H, Me), 1.57 (sext, *J*=7.3 Hz, 2H, CH_2), 2.55 (t, *J*=7.9 Hz, 2H, CH_2), 7.08 (d, *J*=5.2 Hz, 1H), 7.14 (d, *J*=8.3 Hz, 2H), 7.52 (d, *J*=5.2 Hz, 1H), 7.53 (d, *J*=8.3 Hz, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=13.7, 24.1, 38.1, 87.2, 94.8, 116.1, 117.0, 128.9, 133.1, 133.4, 133.9, 138.0, 146.5, 168.2; GC–MS (EI, 70 eV): *m*/*z* (%)=334 (M^+, ^{81}Br, 57), 332 (M^+, ^{79}Br, 57), 306 (27), 277 (100), 195 (18), 171 (16), 152 (14), 142 (13), 114 (12); HRMS (ESI): calcd for $C_{16}H_{13}{}^{79}BrOS$ 331.98650, found 331.98693 and calcd for $C_{16}H_{13}{}^{81}BrOS$ 333.98445, found 333.98496; IR (ATR, cm^{-1}): ν=3370 (w), 3103 (w), 3083 (w), 2956 (m), 2927 (m), 2868 (m), 2547 (w), 2431 (w), 2273 (w), 2189 (s), 1913 (w), 1625 (m), 1592 (s), 1488 (s), 1463 (w), 1397 (s), 1352 (m), 1302 (m), 1277 (m), 1188 (m), 1174 (s), 1148 (m), 1114 (w), 1085 (w), 1009 (m), 967 (m), 903 (w), 879 (s).

6.4. 1-(3-Bromothiophen-2-yl)-3-(4-methoxyphenyl)prop-2-yn-1-one (1d)

Yellow solid, yield 70%, mp 98–100 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ=3.78 (s, 3H, MeO), 6.86 (d, *J*=8.9 Hz, 2H), 7.07 (d, *J*=5.2 Hz, 1H), 7.52 (d, *J*=5.2 Hz, 1H), 7.57 (d, *J*=8.9 Hz, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=55.4, 87.4, 95.4, 111.7, 114.4, 115.9, 132.7, 133.2, 133.4, 133.8, 161.9, 165.1; GC–MS (EI, 70 eV): *m*/*z* (%)=322 (M^+, ^{81}Br, 100), 320 (M^+, ^{79}Br, 99), 294 (58), 277 (68), 251 (16), 169 (21), 159 (62), 144 (15), 131 (4), 116 (15); HRMS (ESI): calcd for $C_{14}H_9{}^{79}BrOS$ 319.95011, found 319.95012 and calcd for $C_{14}H_9{}^{81}BrOS$ 321.94807, found 321.94828; IR (ATR, cm^{-1}): ν=3099 (w), 2955 (w), 2841 (w), 2587 (w), 2516 (w), 2188 (s), 1893 (w), 1769 (w), 1715 (w), 1668 (m), 1624 (m), 1596 (m), 1567 (w), 1504 (s), 1445 (w), 1423 (m), 1402 (s), 1349 (m), 1305 (w), 1253 (s), 1186 (w), 1168 (m), 1106 (w), 1083 (w), 1020 (m), 957 (w), 913 (w), 880 (s).

6.5. 1-(3-(4-(Diethylamino)phenylamino)thiophen-2-yl)-3-phenylprop-2-yn-1-one (2h)

Yellow solid, yield 66%, mp 124–126 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.07 (t, *J*=7.1 Hz, 6H, 2Me), 3.25 (q, *J*=7.1 Hz, 4H, $2CH_2$), 6.57 (d, *J*=8.9 Hz, 2H), 6.76 (d, *J*=5.5 Hz, 1H), 7.00 (d, *J*=8.9 Hz, 2H), 7.26–7.35 (m, 4H), 7.54–7.57 (m, 2H), 9.75 (s, 1H, NH); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=12.5, 44.5, 87.6, 90.7, 112.4, 115.0, 117.6, 120.7,

124.4, 128.5, 128.6, 130.1, 132.7, 136.2, 145.6, 155.0, 168.8; GC–MS (EI, 70 eV): *m*/*z* (%)=374 (M^+, 83), 359 (100), 329 (13), 302 (17), 272 (4), 226 (3), 180 (3), 137 (4); HRMS (ESI): calcd for $C_{23}H_{22}N_2OS$ 374.14474, found 374.14445; IR (ATR, cm^{-1}): ν=3276 (w), 3078 (w), 2968 (m), 2927 (w), 2868 (w), 2198 (s), 1611 (m), 1566 (s), 1517 (s), 1488 (m), 1443 (w), 1381 (s), 1264 (s), 1235 (w), 1196 (m), 1154 (m), 1094 (w), 1076 (w), 1025 (w), 1011 (w), 979 (m), 919 (w), 852 (w), 802 (w), 761 (m).

6.6. 1-(3-Bromothiophen-2-yl)-3-(3,5-dimethylphenylamino)-3-phenylprop-2-en-1-one (2h)

Yellow oil, yield 65%, ^1H NMR (250 MHz, $CDCl_3$): δ=2.02 (s, 6H, 2Me), 6.26 (s, 1H), 6.29–6.31 (m, 2H), 6.53–6.55 (m, 1H), 6.96 (d, *J*=5.2 Hz, 1H), 7.21–7.34 (m, 6H), 12.58 (s, 1H, NH); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=21.1, 98.0, 110.3, 121.0, 126.1, 128.3, 128.4, 129.3, 129.8, 133.0, 135.6, 138.3, 138.8, 140.6, 162.1, 180.8; GC–MS (EI, 70 eV): *m*/*z* (%)=413 (M^+, ^{81}Br, 15), 411 (M^+, ^{79}Br, 15), 396 (16), 332 (35), 250 (10), 222 (100), 207 (25), 189 (13), 103 (5), 77 (11); HRMS (ESI): calcd for $C_{21}H_{18}{}^{79}BrNOS$ (M+H) 412.03652, found 412.03621 and calcd for $C_{21}H_{18}{}^{81}BrNOS$ (M+H) 414.03462, found 414.03422; IR (ATR, cm^{-1}): ν=3101 (w), 3087 (w), 2915 (w), 1602 (w), 1581 (m), 1538 (s), 1513 (w), 1481 (m), 1443 (w), 1408 (s), 1347 (w), 1308 (s), 1278 (w), 1254 (m), 1205 (m), 1170 (m), 1113 (w), 1085 (w), 1024 (w), 996 (m), 948 (w), 897 (w), 870 (m), 852 (s).

6.7. 4,5-Diphenylthieno[3,2-*b*]pyridin-7(4*H*)-one (3a)

Yellow solid, yield 78%, mp 233–235 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=6.35 (s, 1H), 6.52 (d, *J*=5.5 Hz, 1H), 7.06–7.14 (m, 7H), 7.20–7.30 (m, 3H), 7.46 (d, *J*=5.5 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=113.4, 118.9, 128.0, 128.3, 128.6, 128.7, 129.0, 129.4, 129.5, 131.4, 134.6, 140.1, 146.5, 151.7, 173.8; GC–MS (EI, 70 eV): *m*/*z* (%)=303 (M^+, 100), 275 (43), 241 (4), 171 (16), 136 (3), 121 (6), 102 (4), 77 (8); HRMS (ESI): calcd for $C_{19}H_{13}NOS$ (M+H) 304.07906, found 304.07893; IR (ATR, cm^{-1}): ν=3108 (w), 3039 (w), 2917 (w), 2850 (w), 1609 (m), 1591 (s), 1574 (m), 1513 (w), 1480 (s), 1451 (m), 1442 (m), 1423 (w), 1384 (m), 1312 (m), 1276 (m), 1249 (m), 1185 (m), 1158 (m), 1113 (m), 1099 (m), 1067 (m), 1049 (m), 1026 (m), 998 (w), 978 (w), 930 (m), 876 (w), 853 (w), 829 (m), 754 (s).

6.8. 5-Phenyl-4-*p*-tolylthieno[3,2-*b*]pyridin-7(4*H*)-one (3b)

Yellow solid, yield 80%, mp 203–205 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=2.23 (s, 3H, Me), 6.35 (s, 1H), 6.52 (d, *J*=5.5 Hz, 1H), 6.95 (d, *J*=8.4 Hz, 2H), 7.04 (d, *J*=8.1 Hz, 2H), 7.07–7.15 (m, 5H), 7.44 (d, *J*=5.5 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=21.1, 113.4, 119.0, 128.0, 128.2, 128.5, 128.7, 129.3, 130.1, 131.3, 134.7, 137.5, 139.0, 146.7, 151.8, 173.8; GC–MS (EI, 70 eV): *m*/*z* (%)=317 (M^+, 100), 289 (33), 273 (6), 214 (5), 186 (7), 171 (12), 137 (4), 102 (5); HRMS (ESI): calcd for $C_{20}H_{15}NOS$ (M+H) 318.09471, found 318.09493; IR (ATR, cm^{-1}): ν=3107 (w), 3051 (w), 2918 (w), 2859 (w), 1607 (m), 1599 (s), 1512 (m), 1480 (s), 1441 (m), 1425 (w), 1384 (m), 1313 (m), 1276 (m), 1250 (w), 1185 (w), 1154 (w), 1112 (m), 1100 (m), 1046 (m), 999 (w), 976 (w), 928 (m), 914 (w), 879 (w), 827 (s), 755 (s).

6.9. 4-(4-Ethylphenyl)-5-phenylthieno[3,2-*b*]pyridin-7(4*H*)-one (3c)

Yellow solid, yield 82%, mp 204–206 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=1.13 (t, *J*=7.6 Hz, 3H, Me), 2.56 (q, *J*=7.6 Hz, 2H, CH_2), 6.50 (s, 1H), 6.57 (d, *J*=5.5 Hz, 1H), 6.99 (d, *J*=8.4 Hz, 2H), 7.07–7.16 (m, 7H), 7.51 (d, *J*=5.5 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=15.1, 28.3, 113.2, 119.0, 128.0, 128.2, 128.7, 128.8, 129.4, 129.8, 131.7, 134.6, 137.6, 145.4, 146.9, 152.1, 173.5; GC–MS (EI, 70 eV): *m*/*z* (%)=331 (M^+, 100), 303 (21), 288 (8), 274 (6); HRMS (ESI): calcd for $C_{21}H_{17}NOS$ (M+H) 332.11030, found 332.11020; IR (ATR, cm^{-1}): ν=3116 (w), 3052 (w), 2919 (w), 1597 (s), 1480 (m), 1435 (w), 1385 (w), 1312 (w), 1274 (w), 1112 (m), 1010 (m), 1046 (m), 834 (m), 700 (s).

6.10. 4-(4-Methoxyphenyl)-5-phenylthieno[3,2-*b*]pyridin-7(4*H*)-one (3d)

Yellow solid, yield 78%, mp 210–212 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=3.70 (s, 3H, MeO), 6.34 (s, 1H), 6.53 (d, *J*=5.5 Hz, 1H), 6.75 (d, *J*=9.0 Hz, 2H), 7.00 (d, *J*=9.0 Hz, 2H), 7.07–7.20 (m, 5H), 7.46 (d, *J*=5.5 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=55.4, 113.4, 114.5, 119.0, 128.0, 128.5, 128.7, 129.4, 129.6, 131.3, 132.8, 134.8, 147.0, 152.0, 159.4, 173.8; GC–MS (EI, 70 eV): *m*/*z* (%)=333 (M^+, 100), 305 (14), 290 (10), 260 (4), 216 (6), 188 (9), 160 (8), 134 (4), 116 (3), 102 (5); HRMS (ESI): calcd for $C_{20}H_{15}NO_2S$ (M+H) 334.08963, found 334.09029; IR (ATR, cm^{-1}): ν=3100 (w), 3047 (w), 3011 (w), 2962 (w), 2836 (w), 1599 (s), 1577 (m), 1505 (s), 1478 (s), 1381 (m), 1317 (w), 1297 (m), 1240 (s), 1176 (m), 1104 (m), 1075 (w), 1067 (w), 1046 (m), 1022 (m), 1011 (m), 973 (w), 946 (w), 919 (m), 881 (w), 833 (s), 754 (s).

6.11. 4-(4-Ethoxyphenyl)-5-phenylthieno[3,2-*b*]pyridin-7(4*H*)-one (3e)

Yellow solid, yield 82%, mp 182–184 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=1.31 (t, *J*=7.0 Hz, 3H, Me), 3.91 (q, *J*=7.0 Hz, 2H, CH_2O), 6.36 (s, 1H), 6.54 (d, *J*=5.5 Hz, 1H), 6.73 (d, *J*=8.9 Hz, 2H), 7.0 (d, *J*=9.0 Hz, 2H), 7.07–7.16 (m, 5H), 7.46 (d, *J*=5.5 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=13.6, 62.7, 112.3, 113.9, 118.0, 127.0, 127.4, 127.6, 128.3, 128.5, 130.3, 131.6, 133.7, 146.0, 151.0, 157.9, 172.8; GC–MS (EI, 70 eV): *m*/*z* (%)=347 (M^+, 100), 319 (12), 318 (10), 216 (10), 188 (6); HRMS (ESI): calcd for $C_{21}H_{17}NO_2S$ (M+H) 348.10528, found 348.10526; IR (ATR, cm^{-1}): ν=3099 (w), 3052 (w), 2973 (w), 2928 (w), 1606 (m), 1588 (m), 1509 (m), 1474 (s), 1442 (w), 1379 (m), 1234 (m), 1177 (w), 1105 (w), 1046 (m), 842 (m), 756 (s), 703 (s).

6.12. 4-(2,4-Dimethoxyphenyl)-5-phenylthieno[3,2-*b*]pyridin-7(4*H*)-one (3f)

Yellow gel, yield 70%. ^1H NMR (300 MHz, $CDCl_3$): δ=2.75 (s, 3H, MeO), 3.59 (s, 3H, MeO), 6.35 (d, *J*=2.6 Hz, 1H), 6.39 (dd, *J*=8.4, 2.6 Hz, 1H), 6.40 (s, 1H), 6.53 (d, *J*=5.5 Hz, 1H), 7.02 (d, *J*=8.6 Hz, 1H), 7.16–7.22 (m, 5H), 7.50 (d, *J*=5.5 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=55.4, 55.5, 99.2, 104.6, 113.0, 118.9, 121.9, 127.7, 128.3, 128.7, 130.1, 131.2, 134.9, 147.1, 152.9, 155.5, 161.3, 171.0, 174.1; GC–MS (EI, 70 eV): *m*/*z* (%)=363 (M^+, 100), 335 (8), 320 (4), 304 (3), 289 (3), 276 (4), 260 (5), 218 (3), 175 (4), 130 (5); HRMS (ESI): calcd for $C_{21}H_{17}NO_3S$ (M+H) 364.10019, found 364.10074; IR (ATR, cm^{-1}): ν=3057 (w), 3004 (w), 2935 (w), 2837 (w), 1732 (w), 1587 (s), 1507 (s), 1476 (s), 1438 (m), 1420 (m), 1384 (m), 1324 (w), 1304 (m), 1280 (m), 1244 (m), 1207 (s), 1159 (m), 1136 (w), 1110 (m), 1067 (w), 1048 (s), 1023 (s), 923 (m), 907 (m), 835 (s).

6.13. 5-Phenyl-4-(3,4,5-trimethoxyphenyl)thieno[3,2-*b*]pyridin-7(4*H*)-one (3g)

Yellow solid, yield 80%, mp 231–232 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=3.61 (s, 6H, 2MeO), 3.78 (s, 3H, MeO), 6.34 (s, 1H), 6.36 (s, 2H), 6.70 (d, *J*=5.5 Hz, 1H), 7.13–7.20 (m, 5H), 7.51 (d, *J*=5.5 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=56.4, 61.0, 106.3, 113.3, 119.0, 128.0, 128.5, 128.9, 129.0, 131.5, 134.8, 135.4, 138.3, 146.4, 151.7, 153.4, 173.6; GC–MS (EI, 70 eV): *m*/*z* (%)=393 (M^+, 100), 378 (37), 205 (10), 276 (6); HRMS (ESI): calcd for $C_{22}H_{19}NO_4S$ (M+H) 394.11070, found 394.11110; IR (ATR, cm^{-1}): ν=3116 (w), 3058 (w), 2969 (w), 2928 (w), 2840 (w), 1598 (s), 1578 (s), 1501 (m), 1468 (s), 1442 (w),

1417 (s), 1385 (w), 1237 (s), 1178 (w), 1123 (s), 1107 (w), 1010 (m), 842 (m), 773 (m), 756 (s), 702 (s), 695 (s).

6.14. 4-(4-(Diethylamino)phenyl)-5-phenylthieno[3,2-*b*]pyridin-7(4*H*)-one (3h)

Yellow solid, yield 80%, mp 194–196 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.06 (t, J=7.2 Hz, 6H, 2Me), 3.24 (q, J=7.0 Hz, 4H, $2CH_2$), 6.38 (s, 1H), 6.43 (d, J=9.1 Hz, 2H), 6.63 (d, J=5.5 Hz, 1H), 6.84 (d, J=9.1 Hz, 2H), 7.11–7.19 (m, 5H, Ph), 7.46 (d, J=5.5 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=11.3, 43.3, 110.3, 112.2, 118.4, 126.8, 126.9, 127.4, 127.7, 128.0, 128.4, 130.0, 134.1, 146.5, 146.6, 151.4, 172.8; GC–MS (EI, 70 eV): m/z (%)=374 (M^+, 67), 359 (100), 330 (9), 302 (8), 273 (3), 228 (3), 171 (6), 136 (4); HRMS (ESI): calcd for $C_{23}H_{22}N_2OS$ 374.14474, found 374.14439; IR (ATR, cm^{-1}): ν=3541 (w), 3389 (w), 3050 (m), 2963 (m), 2925 (w), 1609 (s), 1591 (s), 1517 (s), 1475 (s), 1444 (w), 1422 (w), 1405 (w), 1377 (m), 1355 (m), 1317 (m), 1264 (s), 1197 (m), 1156 (m), 1108 (m), 1073 (m), 1048 (s), 1016 (w), 915 (w), 817 (m), 771 (s).

6.15. 4-(4-Fluorophenyl)-5-phenylthieno[3,2-*b*]pyridin-7(4*H*)-one (3i)

Yellow solid, yield 83%, mp 183–185 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ=6.33 (s, 1H), 6.51 (d, J=5.5 Hz, 1H), 6.93–6.98 (m, 2H), 7.06–7.20 (m, 7H), 7.48 (d, J=5.5 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=113.5, 116.5 (d, J=23.0 Hz), 128.1, 128.6, 128.9, 129.4, 129.6, 130.4 (d, J=8.8 Hz), 131.6, 134.4, 136.1 (d, J=3.4 Hz), 146.5, 151.7, 162.1 (d, J=250.6 Hz), 173.8; ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−110.7 (s, CF); GC–MS (EI, 70 eV): m/z (%)=321 (M^+, 100), 293 (40), 259 (3), 219 (4), 189 (10), 171 (8), 139 (4), 121 (4), 102 (4), 95 (5); HRMS (ESI): calcd for $C_{19}H_{12}FNOS$ (M+H) 322.06964, found 322.06965; IR (ATR, cm^{-1}): ν=3099 (w), 3061 (w), 2921 (w), 2851 (w), 1595 (s), 1574 (m), 1538 (w), 1504 (s), 1477 (s), 1441 (m), 1410 (w), 1380 (m), 1310 (m), 1295 (w), 1274 (w), 1234 (w), 1211 (s), 1151 (m), 1113 (m), 1099 (m), 1066 (m), 1041 (m), 996 (w), 958 (w), 929 (w), 912 (w), 881 (w), 844 (s), 832 (s).

6.16. 5-Phenyl-4-(3-trifluoromethylphenyl)thieno[3,2-*b*]pyridin-7(4*H*)-one (3j)

Yellow solid, yield 81%, mp 250–252 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=6.36 (s, 1H), 6.51 (d, J=5.5 Hz, 1H), 7.04–7.17 (m, 5H), 7.35–7.47 (m, 4H), 7.51 (d, J=5.5 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=113.7, 118.3, 123.0 (q, J=272.8 Hz), 125.8 (m, 2C), 128.2, 128.8, 129.0, 129.3, 132.0 (q, J=33.4 Hz), 132.1, 132.2, 132.3, 134.1, 140.6, 145.9, 151.4, 173.8; ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−62.9 (s, CF_3); GC–MS (EI, 70 eV): m/z (%)=371 (M^+, 100), 343 (45), 273 (4), 241 (3), 171 (13), 145 (7), 121 (3); HRMS (ESI): calcd for $C_{20}H_{12}F_3NOS$ (M+H) 372.06645, found 372.06613; IR (ATR, cm^{-1}): ν=3107 (w), 3047 (w), 2922 (w), 1606 (s), 1578 (m), 1537 (w), 1516 (w), 1480 (m), 1444 (m), 1379 (m), 1330 (s), 1264 (w), 1250 (w), 1234 (w), 1191 (m), 1169 (m), 1156 (w), 1115 (s), 1095 (s), 1075 (m), 1051 (m), 1001 (w), 980 (w), 938 (w), 920 (m), 878 (w), 859 (w), 837 (m), 811 (m), 779 (s).

6.17. 4-(3-Bromophenyl)-5-phenylthieno[3,2-*b*]pyridin-7(4*H*)-one (3k)

Yellow solid, yield 78%, mp 206–208 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=6.33 (s, 1H), 6.53 (d, J=5.5 Hz, 1H), 7.04–7.18 (m, 7H), 7.28–7.30 (m, 1H), 7.36–7.40 (m, 1H), 7.49 (d, J=5.5 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=113.6, 118.6, 122.7, 127.4, 128.2, 128.6, 129.0, 129.3, 130.7, 131.7, 131.8, 132.2, 134.2, 141.1, 146.0, 151.4, 173.7; GC–MS (EI, 70 eV): m/z (%)=383 (M^+, ^{81}Br, 100), 381 (M^+, ^{79}Br, 97), 355 (37), 300 (6), 273 (13), 241 (4), 200 (6), 171 (20), 137 (11), 120 (12), 102 (9), 76 (8); HRMS (ESI): calcd for $C_{19}H_{12}{}^{79}BrNOS$ (M+H) 381.98957, found 381.98951 and calcd for $C_{19}H_{12}{}^{81}BrNOS$ (M+H) 383.98763, found 383.98752; IR (ATR, cm^{-1}): ν=3107 (w), 3050 (w), 2917 (w), 2858 (w), 1732 (w), 1609 (m), 1599 (m), 1572 (s), 1515 (w), 1474 (s), 1443 (w), 1418 (w), 1380 (m), 1312 (m), 1277 (w), 1249 (w), 1185 (w), 1138 (w), 1101 (m), 1065 (m), 1048 (m), 1029 (w), 997 (w), 980 (w), 928 (w), 877 (w), 858 (w), 834 (m), 776 (m).

6.18. 4-(4-Nitrophenyl)-5-phenylthieno[3,2-*b*]pyridin-7(4*H*)-one (3l)

Yellow solid, yield 86%, mp 210–212 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=6.41 (s, 1H), 6.54 (d, J=5.5 Hz, 1H), 7.08–7.22 (m, 5H), 7.36 (d, J=9.0 Hz, 2H), 7.55 (d, J=5.5 Hz, 1H), 8.15 (d, J=9.0 Hz, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=114.0, 118.0, 124.8, 128.5, 128.7, 128.9, 129.3, 129.4, 129.9, 132.4, 133.9, 145.4, 147.3, 151.0, 173.6; GC–MS (EI, 70 eV): m/z (%)=348 (M^+, 100), 320 (24), 274 (18), 273 (10), 172 (7); HRMS (ESI): calcd for $C_{19}H_{12}N_2O_3S$ (M+H) 349.06414, found 349.06436; IR (ATR, cm^{-1}): ν=3088 (w), 3054 (w), 1587 (s), 1574 (s), 1509 (m), 1486 (s), 1474 (s), 1443 (w), 1307 (m), 1103 (w), 1088 (m), 1041 (w), 827 (m), 730 (m), 697 (s).

6.19. 4-(4-Methylbenzyl)-5-phenylthieno[3,2-*b*]pyridin-7(4*H*)-one (3m)

Yellow solid, yield 90%, mp 237–239 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.23 (s, 3H, Me), 5.11 (s, 2H, CH_2), 6.26 (s, 1H), 6.74 (d, J=8.0 Hz, 2H), 6.87 (d, J=5.5 Hz, 1H), 7.01 (d, J=7.9 Hz, 2H), 7.22–7.36 (m, 5H), 7.51 (d, J=5.5 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=21.0, 53.5, 113.7, 118.0, 125.4, 128.5, 128.6, 129.6, 129.7, 129.9, 132.0, 132.9, 134.4, 137.6, 145.5, 152.6, 173.6; GC–MS (EI, 70 eV): m/z (%)=331 (M^+, 44), 198 (6), 171 (3), 105 (100), 77 (13); HRMS (ESI): calcd for $C_{21}H_{17}NOS$ (M+H) 332.11036, found 332.11069; IR (ATR, cm^{-1}): ν=3107 (w), 3052 (w), 3020 (w), 2920 (w), 2852 (w), 1597 (s), 1567 (m), 1537 (w), 1515 (w), 1498 (s), 1442 (m), 1427 (w), 1416 (w), 1389 (m), 1347 (m), 1311 (m), 1297 (m), 1244 (m), 1224 (w), 1208 (m), 1123 (w), 1099 (s), 1068 (m), 1034 (w), 998 (w), 969 (m), 920 (m), 858 (w), 831 (s).

6.20. 4-(3-Methoxybenzyl)-5-phenylthieno[3,2-*b*]pyridin-7(4*H*)-one (3n)

Yellow solid, yield 92%, mp 122–124 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.63 (s, 3H, MeO), 5.11 (s, 2H, CH_2), 6.26 (s, 1H), 6.39–6.34 (m, 1H), 6.42–6.45 (m, 1H), 6.69–6.72 (m, 1H), 6.88 (d, J=5.5 Hz, 1H), 7.10–7.15 (m, 1H), 7.23–7.36 (m, 5H), 7.51 (d, J=5.5 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=53.6, 55.1, 111.6, 112.8, 113.7, 117.7, 117.9, 128.5, 128.7, 129.6, 129.8, 130.1, 132.0, 134.3, 137.6, 145.5, 152.5, 160.0, 173.5; GC–MS (EI, 70 eV): m/z (%)=347 (M^+, 71), 198 (3), 171 (2), 121 (100), 91 (19), 78 (10), 65 (5); HRMS (ESI): calcd for $C_{21}H_{17}NO_2S$ (M+H) 348.10528, found 348.10534; IR (ATR, cm^{-1}): ν=3108 (w), 3057 (w), 2956 (w), 2831 (w), 1738 (w), 1604 (m), 1589 (s), 1516 (w), 1492 (s), 1457 (w), 1434 (m), 1386 (m), 1354 (w), 1314 (w), 1289 (m), 1255 (m), 1202 (m), 1182 (w), 1158 (m), 1105 (s), 1078 (w), 1069 (w), 1035 (m), 993 (w), 960 (m), 949 (w), 916 (w), 876 (w), 845 (s).

6.21. 4-Phenethyl-5-phenylthieno[3,2-*b*]pyridin-7(4*H*)-one (3o)

Yellow solid, yield 91%, mp 70–72 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.81 (t, J=7.5 Hz, 2H, CH_2), 4.13 (t, J=7.5 Hz, 2H, CH_2), 6.24 (s, 1H), 6.64–6.67 (m, 2H), 7.07–7.11 (m, 5H), 7.17 (d, J=5.5 Hz, 1H), 7.31–7.41 (m, 3H), 7.68 (d, J=5.5 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=35.6, 51.5, 113.6, 117.0, 127.0, 128.5, 128.6, 128.7, 128.8, 129.4, 130.0, 132.3, 134.5, 136.5, 144.8, 152.1, 173.3; GC–MS (EI,

70 eV): *m*/*z* (%)=240 (M^+, 100), 331 (44), 138 (18), 241 (17); HRMS (ESI): calcd for $C_{21}H_{17}NOS$ (M+H) 332.11030, found 332.11020; IR (ATR, cm^{-1}): ν=3492 (w), 3053 (w), 1581 (s), 1533 (m), 1493 (m), 1441 (w), 1359 (w), 1304 (w), 1193 (m), 1105 (m), 846 (w), 750 (s), 698 (s).

6.22. 4-Cyclohexyl-5-phenylthieno[3,2-*b*]pyridin-7(4*H*)-one (3p)

Yellow solid, yield 90%, mp 231–233 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=0.89–2.24 (m, 10H), 6.13 (s, 1H), 7.25–7.28 (m, 2H), 7.38–7.43 (m, 4H), 7.45 (d, *J*=5.6 Hz, 1H), 7.62 (d, *J*=5.6 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=24.9, 25.9, 30.5, 62.4, 113.4, 119.3, 127.9, 128.8, 129.3, 130.8, 132.3, 136.0, 143.22, 152.8, 173.0; GC–MS (EI, 70 eV): *m*/*z* (%)=309 (M^+, 48), 227 (100), 199 (14), 171 (4), 154 (3), 96 (3); HRMS (ESI): calcd for $C_{19}H_{19}NOS$ (M+H) 310.12602, found 310.12561; IR (ATR, cm^{-1}): ν=3080 (w), 2932 (w), 2856 (w), 1737 (w), 1604 (m), 1592 (s), 1538 (w), 1511 (w), 1481 (s), 1447 (m), 1425 (w), 1389 (m), 1347 (w), 1336 (m), 1308 (m), 1253 (m), 1194 (w), 1175 (m), 1149 (w), 1101 (s), 1067 (m), 1019 (w), 997 (m), 934 (w), 897 (w), 872 (w), 845 (s).

6.23. 4-Heptyl-5-phenylthieno[3,2-*b*]pyridin-7(4*H*)-one (3q)

Yellow gel, yield 89%. ^1H NMR (300 MHz, $CDCl_3$): δ=0.75 (t, *J*=7.1 Hz, 3H, Me), 1.02–1.59 (m, 9H), 3.89 (t, *J*=8.0 Hz, 2H, CH_2), 6.19 (s, 1H), 7.11 (d, *J*=5.5 Hz, 1H), 7.28–7.32 (m, 2H), 7.41–7.43 (m, 3H), 7.67 (d, *J*=5.5 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=12.9, 21.3, 25.2, 27.4, 28.4, 30.3, 49.3, 112.5, 116.1, 127.6, 127.7, 128.4, 128.8, 131.1, 133.7, 144.0, 151.0, 172.2; IR (ATR, cm^{-1}): ν=3057 (w), 2921 (m), 2856 (w), 1737 (w), 1581 (s), 1535 (s), 1493 (m), 1466 (w), 1370 (w), 1299 (w), 1193 (m), 1099 (s), 1019 (w), 845 (m), 768 (s), 703 (s).

6.24. 4-(4-Methoxyphenyl)-5-*p*-tolylthieno[3,2-*b*]pyridin-7(4*H*)-one (3r)

Yellow solid, yield 82%, mp 175–177 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=2.20 (s, 3H, Me), 3.73 (s, 3H, MeO), 6.36 (s, 1H), 6.53 (d, *J*=5.5 Hz, 1H), 6.76 (d, *J*=9.0 Hz, 2H), 6.92–7.02 (m, 6H), 7.46 (d, *J*=5.5 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=21.1, 55.4, 113.4, 114.5, 118.9, 128.5, 128.7, 129.2, 129.5, 131.2, 131.9, 133.0, 138.6, 147.0, 152.1, 159.4, 173.9; GC–MS (EI, 70 eV): *m*/*z* (%)=347 (M^+, 100), 319 (17), 304 (8), 276 (3), 260 (3), 216 (7), 188 (10), 160 (8), 134 (4), 115 (7); HRMS (ESI): calcd for $C_{21}H_{17}NO_2S$ (M+H) 348.10528, found 348.10517; IR (ATR, cm^{-1}): ν=3086 (w), 3044 (w), 3005 (w), 2963 (w), 2916 (w), 2838 (w), 1737 (w), 1599 (s), 1585 (m), 1537 (w), 1506 (s), 1478 (m), 1380 (m), 1313 (w), 1297 (m), 1274 (w), 1244 (s), 1176 (m), 1147 (w), 1105 (m), 1068 (w), 1046 (m), 973 (w), 915 (w), 878 (w), 837 (m), 825 (s).

6.25. 4-(4-Fluorophenyl)-5-*p*-tolylthieno[3,2-*b*]pyridin-7(4*H*)-one (3s)

Yellow solid, yield 85%, mp 215–217 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=2.15 (s, 3H, Me), 6.28 (s, 1H), 6.48 (d, *J*=5.5 Hz, 1H), 6.90–6.98 (m, 6H), 7.08–7.13 (m, 2H), 7.44 (d, *J*=5.5 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=21.1, 113.4, 116.5 (d, *J*=23.0 Hz), 118.7, 128.4, 128.8, 129.2, 130.4 (d, *J*=8.8 Hz), 131.5, 131.6, 136.5 (d, *J*=3.3 Hz), 138.9, 146.4, 151.8, 162.9 (d, *J*=250.3 Hz), 173.7; ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−110.9 (s, CF); GC–MS (EI, 70 eV): *m*/*z* (%)=335 (M^+, 100), 307 (41), 291 (5), 219 (6), 190 (6), 171 (4), 146 (5), 115 (5), 95 (4); HRMS (ESI): calcd for $C_{20}H_{14}FNOS$ (M+H) 336.08529, found 336.08595; IR (ATR, cm^{-1}): ν=3116 (w), 3040 (w), 2919 (w), 2872 (w), 1603 (m), 1595 (s), 1524 (w), 1495 (m), 1479 (s), 1424 (w), 1415 (w), 1384 (m), 1315 (m), 1276 (w), 1254 (w), 1214 (m), 1184 (m), 1158 (m), 1101 (m), 1066 (m), 1041 (m), 1017 (m), 971 (w), 950 (w), 914 (w), 887 (w), 835 (m), 818 (s).

6.26. 4-(4-Chlorophenyl)-5-*p*-tolylthieno[3,2-*b*]pyridin-7(4*H*)-one (3t)

Yellow solid, yield 78%, mp 104–106 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=2.19 (s, 3H, Me), 6.30 (s, 1H), 6.50 (d, *J*=5.5 Hz, 1H), 6.91 (d, *J*=9.1 Hz, 2H), 6.97 (d, *J*=9.1 Hz, 2H), 7.04 (d, *J*=8.7 Hz, 2H), 7.24 (d, *J*=8.7 Hz, 2H), 7.46 (d, *J*=5.5 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=20.2, 112.5, 115.4, 117.6, 119.1, 127.7, 127.9, 128.2, 128.7, 128.9, 130.7, 133.9, 138.1, 145.2, 150.7, 172.8; GC–MS (EI, 70 eV): *m*/*z* (%)=353 (M^+, ^{37}Cl, 36), 351 (M^+, ^{35}Cl, 100), 323 (38), 286 (3), 273 (5), 235 (3), 200 (8), 172 (12), 137 (12), 115 (7); HRMS (ESI): calcd for $C_{20}H_{14}ClNOS$ (M+H) 353.04846, found 353.04852; IR (ATR, cm^{-1}): ν=3270 (w), 3188 (w), 3033 (w), 2917 (w), 2860 (w), 1731 (w), 1587 (s), 1506 (m), 1475 (s), 1424 (w), 1404 (w), 1377 (m), 1332 (w), 1307 (m), 1271 (w), 1251 (w), 1242 (w), 1184 (w), 1171 (w), 1089 (m), 1067 (w), 1041 (m), 1014 (m), 947 (w), 914 (w), 818 (s).

6.27. 4-Phenyl-5-(4-propylphenyl)thieno[3,2-*b*]pyridin-7(4*H*)-one (3u)

Yellow solid, yield 83%, mp 141–143 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=0.75 (t, *J*=7.4 Hz, 3H, Me), 1.46 (sext, *J*=7.4 Hz, 2H, CH_2), 2.39 (t, *J*=7.9 Hz, 2H, CH_2), 6.35 (s, 1H), 6.51 (d, *J*=5.5 Hz, 1H), 6.89 (d, *J*=8.3 Hz, 2H), 6.96 (d, *J*=8.3 Hz, 2H), 7.05–7.08 (m, 2H), 7.21–7.29 (m, 3H), 7.43 (d, *J*=5.5 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=13.5, 24.0, 37.4, 113.3, 118.9, 128.0, 128.5, 128.6, 128.8, 129.2, 129.4, 131.2, 131.9, 140.2, 143.4, 146.4, 151.8, 173.8; GC–MS (EI, 70 eV): *m*/*z* (%)=345 (M^+, 100), 317 (12), 288 (49), 272 (3), 254 (2), 201 (3), 172 (4), 136 (3), 115 (3); HRMS (ESI): calcd for $C_{22}H_{19}NOS$ (M+H) 346.12602, found 346.12579; IR (ATR, cm^{-1}): ν=3120 (w), 3050 (w), 2954 (w), 2928 (w), 2856 (w), 1601 (m), 1587 (s), 1520 (w), 1478 (s), 1453 (m), 1410 (m), 1382 (m), 1338 (w), 1312 (m), 1270 (m), 1206 (w), 1184 (w), 1164 (w), 1107 (m), 1044 (m), 1019 (w), 1000 (w), 961 (w), 916 (w), 871 (w), 829 (s), 759 (s).

6.28. 4-(3-Fluorophenyl)-5-(4-propylphenyl)thieno[3,2-*b*]pyridin-7(4*H*)-one (3v)

Yellow solid, yield 81%, mp 138–140 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=0.75 (t, *J*=7.4 Hz, 3H, Me), 1.46 (sext, *J*=7.3 Hz, 2H, CH_2), 2.40 (t, *J*=7.9 Hz, 2H, CH_2), 6.31 (s, 1H), 6.53 (d, *J*=5.5 Hz, 1H), 6.81–6.85 (m, 1H), 6.90–6.99 (m, 6H), 7.21–7.29 (m, 1H), 7.45 (d, *J*=5.5 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=12.6, 23.0, 36.5, 112.4, 115.8 (d, *J*=20.8 Hz), 115.30 (d, *J*=23.1 Hz), 117.6, 123.7 (d, *J*=3.3 Hz), 127.2, 127.5, 128.1, 129.7 (d, *J*=9.0 Hz), 130.6 (2C), 140.4 (d, *J*=9.6 Hz), 142.7, 145.0, 150.6, 161.5 (d, *J*=250.2 Hz), 172.7; ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−110.0 (s, CF); GC–MS (EI, 70 eV): *m*/*z* (%)=363 (M^+, 100), 335 (12), 306 (48), 272 (2), 219 (3), 191 (3), 139 (3), 115 (5); HRMS (ESI): calcd for $C_{22}H_{18}FNOS$ (M+H) 364.11659, found 364.11671; IR (ATR, cm^{-1}): ν=3114 (w), 3033 (w), 2958 (w), 2926 (w), 2869 (w), 1615 (m), 1593 (s), 1524 (w), 1480 (s), 1412 (w), 1377 (m), 1340 (w), 1317 (m), 1285 (w), 1269 (w), 1256 (w), 1242 (w), 1186 (s), 1155 (w), 1100 (m), 1077 (m), 1046 (m), 1005 (w), 975 (w), 910 (w), 876 (m), 835 (s).

6.29. 4-(3,5-Dichlorophenyl)-5-(4-propylphenyl)thieno[3,2-*b*]pyridin-7(4*H*)-one (3w)

Yellow solid, yield 85%, mp 80–82 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=0.02 (t, *J*=7.3 Hz, 3H, Me), 0.74 (sext, *J*=7.6 Hz, 2H, CH_2), 1.69 (t, *J*=7.9 Hz, 2H, CH_2), 5.57 (s, 1H), 5.80 (d, *J*=5.5 Hz, 1H), 6.21–6.23 (m, 4H), 6.26 (d, *J*=1.8 Hz, 2H), 7.48 (t, *J*=1.8 Hz, 1H), 6.76 (d, *J*=5.5 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=13.5, 24.0, 37.5,

113.7, 118.2, 127.4, 128.5, 128.8, 129.1, 129.3, 131.1, 132.0, 135.7, 141.8, 144.1, 145.6, 151.4, 173.8; GC–MS (EI, 70 eV): *m*/*z* (%)=417 (M^+, ^{37}Cl, ^{37}Cl, 14), 415 (M^+, ^{37}Cl, ^{35}Cl, 74), 413 (M^+, ^{35}Cl, ^{35}Cl, 100), 385 (10), 356 (44), 320 (4), 284 (3), 234 (5), 206 (10), 171 (3), 136 (3), 115 (6); HRMS (ESI): calcd for $C_{22}H_{17}Cl_2NOS$ (M+H) 414.04807, found 414.04721; IR (ATR, cm^{-1}): *ν*=3050 (w), 2958 (w), 2927 (w), 2867 (w), 1605 (m), 1568 (s), 1522 (w), 1496 (w), 1475 (m), 1422 (m), 1374 (m), 1338 (w), 1309 (m), 1257 (m), 1202 (w), 1185 (w), 1103 (m), 1061 (s), 1020 (w), 996 (w), 929 (w), 907 (w), 831 (m), 800 (s).

6.30. 5-(4-Methoxyphenyl)-4-*p*-tolylthieno[3,2-*b*]pyridin-7(4*H*)-one (3x)

Yellow solid, yield 80%, mp 172–174 °C. ^1H NMR (300 MHz, $CDCl_3$): *δ*=2.26 (s, 3H, Me), 3.66 (s, 3H, MeO), 6.33 (s, 1H), 6.52 (d, *J*=5.5 Hz, 1H), 6.63 (d, *J*=8.8 Hz, 2H), 6.95 (d, *J*=8.3 Hz, 2H), 7.00 (d, *J*=8.9 Hz, 2H), 7.06 (d, *J*=8.0 Hz, 2H), 7.43 (d, *J*=5.5 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): *δ*=21.1, 55.1, 113.3, 113.4, 119.0, 127.0, 128.2, 128.4, 130.1, 130.7, 131.1, 137.7, 138.9, 146.7, 151.7, 159.6, 173.8; GC–MS (EI, 70 eV): *m*/*z* (%)=347 (M^+, 100), 332 (3), 319 (18), 304 (13), 260 (5), 214 (7), 186 (8), 152 (3), 130 (4); HRMS (ESI): calcd for $C_{21}H_{17}NO_2S$ (M+H) 348.10528, found 348.10458; IR (ATR, cm^{-1}): *ν*=3087 (w), 3063 (w), 2932 (w), 2838 (w), 1737 (w), 1590 (s), 1574 (m), 1510 (m), 1473 (m), 1414 (w), 1376 (m), 1312 (m), 1292 (m), 1269 (w), 1248 (s), 1237 (s), 1175 (m), 1151 (w), 1109 (m), 1070 (w), 1042 (m), 1024 (m), 961 (w), 940 (w), 915 (w), 870 (w), 825 (s).

6.31. 4-(4-Ethylphenyl)-5-(4-methoxyphenyl)thieno[3,2-*b*] pyridin-7(4*H*)-one (3y)

Yellow gel, yield 79%. ^1H NMR (300 MHz, $CDCl_3$): *δ*=1.13 (t, *J*=7.6 Hz, 3H, Me), 2.55 (q, *J*=7.6 Hz, 2H, CH_2), 3.65 (s, 3H, MeO), 6.33 (s, 1H), 6.53 (d, *J*=5.5 Hz, 1H), 6.62 (d, *J*=8.9 Hz, 2H), 6.97 (d, *J*=8.4 Hz, 2H), 6.99 (d, *J*=8.8 Hz, 2H), 7.08 (d, *J*=8.5 Hz, 2H), 7.43 (d, *J*=5.5 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): *δ*=15.1, 28.3, 55.1, 113.3, 113.4, 119.1, 127.0, 128.3, 128.4, 128.8, 130.7, 131.1, 137.8, 145.1, 146.7, 151.7, 159.6, 173.8; GC–MS (EI, 70 eV): *m*/*z* (%)=361 (M^+, 100), 333 (16), 318 (15), 289 (3), 273 (2), 260 (6), 214 (11), 185 (2); HRMS (ESI): calcd for $C_{22}H_{19}NO_2S$ (M+H) 362.12093, found 362.12142; IR (ATR, cm^{-1}): *ν*=3041 (w), 2963 (w), 2930 (w), 2836 (w), 1592 (s), 1496 (m), 1473 (s), 1416 (w), 1377 (m), 1311 (w), 1291 (m), 1272 (w), 1246 (s), 1175 (m), 1105 (m), 1066 (w), 1043 (m), 1027 (m), 968 (w), 915 (w), 829 (s).

6.32. 4-(4-Chlorophenyl)-5-(4-methoxyphenyl)thieno[3,2-*b*] pyridin-7(4*H*)-one (3z)

Yellow solid, yield 82%, mp 84–86 °C. ^1H NMR (300 MHz, $CDCl_3$): *δ*=3.68 (s, 3H, MeO), 6.31 (s, 1H), 6.51 (d, *J*=5.5 Hz, 1H), 6.66 (d, *J*=8.8 Hz, 2H), 6.99 (d, *J*=8.8 Hz, 2H), 7.06 (d, *J*=8.7 Hz, 2H), 7.26 (d, *J*=8.7 Hz, 2H), 7.47 (d, *J*=5.5 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): *δ*=55.2, 113.5, 113.6, 118.6, 126.6, 128.6, 129.8, 129.9, 130.7, 131.5, 134.8, 138.8, 146.2, 151.4, 159.8, 173.8; GC–MS (EI, 70 eV): *m*/*z* (%)= 369 (M^+, ^{37}Cl, 39), 367 (M^+, ^{35}Cl, 100), 339 (20), 324 (18), 289 (2), 260 (10), 235 (7), 200 (11), 172 (12), 152 (4), 130 (4); HRMS (ESI): calcd for $C_{20}H_{14}ClNO_2S$ (M+H) 368.05065, found 368.05043; IR (ATR, cm^{-1}): *ν*=3087 (w), 3050 (w), 2930 (w), 2836 (w), 1731 (w), 1598 (s), 1587 (m), 1574 (m), 1520 (m), 1474 (s), 1403 (w), 1376 (m), 1312 (m), 1292 (m), 1246 (s), 1175 (m), 1103 (m), 1088 (m), 1067 (w), 1026 (m), 914 (w), 828 (s).

6.33. Methyl 3-(phenylethynyl)thiophene-2-carboxylate (4a)

Yellow oil, yield 0.175 g, 72%. ^1H NMR (300 MHz, $CDCl_3$): *δ*=3.85 (s, 3H, MeO), 7.12 (d, *J*=5.1 Hz, 1H), 7.26–7.28 (m, 3H), 7.38 (d, *J*=5.1 Hz, 1H), 7.49–7.52 (m, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): *δ*=51.1, 82.9, 94.2, 121.8, 126.3, 127.3, 127.7, 129.4, 130.8, 131.0, 132.3, 160.8; GC–MS (EI, 70 eV): *m*/*z* (%)=242 (M^+, 100), 227 (72), 211 (40), 199 (23), 184 (7), 171 (13), 139 (52), 113 (8), 105 (7), 91 (6); HRMS (ESI): calcd for $C_{14}H_{10}O_2S$ 242.03960, found 242.03984; IR (ATR, cm^{-1}): *ν*=3100 (m), 2951 (w), 1702 (s), 1596 (w), 1571 (w), 1521 (m), 1505 (w), 1485 (w), 1432 (m), 1408 (m), 1373 (m), 1353 (w), 1288 (m), 1236 (s), 1187 (w), 1097 (m), 1072 (s), 1026 (m), 1003 (w), 994 (m), 934 (m), 878 (m), 845 (m), 784 (s), 755 (s).

6.34. Methyl 3-(*p*-tolylethynyl)thiophene-2-carboxylate (4b)

Yellow oil, yield 0.177 g, 69%. ^1H NMR (300 MHz, $CDCl_3$): *δ*=2.29 (s, 3H, Me), 3.85 (s, 3H, MeO), 7.09 (d, *J*=7.9 Hz, 2H), 7.12 (d, *J*=5.1 Hz, 1H), 7.38 (d, *J*=5.2 Hz, 1H), 7.40 (d, *J*=8.7 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): *δ*=20.5, 51.1, 82.3, 94.6, 118.8, 126.6, 128.1, 129.3, 130.7, 131.0, 132.0, 137.9, 160.8; GC–MS (EI, 70 eV): *m*/*z* (%)=256 (M^+, 100), 241 (79), 225 (27), 213 (28), 197 (6), 185 (9), 169 (5), 139 (5), 112 (9), 98 (6); HRMS (ESI): calcd for $C_{15}H_{12}O_2S$ 256.05525, found 256.05572; IR (ATR, cm^{-1}): *ν*=3108 (w), 2949 (w), 2206 (w), 1708 (s), 1604 (w), 1525 (m), 1502 (m), 1429 (m), 1407 (m), 1376 (m), 1284 (m), 1231 (s), 1182 (w), 1118 (w), 1094 (m), 1072 (s), 1021 (w), 999 (w), 936 (m), 893 (w), 878 (w), 814 (s), 772 (s).

6.35. Methyl 3-(*o*-tolylethynyl)thiophene-2-carboxylate (4c)

Yellow oil, yield 0.175 g, 68%. ^1H NMR (250 MHz, $CDCl_3$): *δ*=2.48 (s, 3H, Me), 3.83 (s, 3H, MeO), 7.08–7.17 (m, 4H), 7.36 (d, *J*=5.1 Hz, 1H), 7.46 (d, *J*=7.6 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): *δ*=20.6, 52.1, 87.6, 94.3, 122.6, 125.5, 127.4, 128.8, 129.5, 130.4, 131.3, 132.3, 132.9, 140.6, 161.8; GC–MS (EI, 70 eV): *m*/*z* (%)=256 (M^+, 43), 241 (43), 224 (56), 213 (100), 195 (46), 184 (19), 165 (8), 152 (44), 139 (8), 127 (8), 112 (14), 98 (8); HRMS (ESI): calcd for $C_{15}H_{12}O_2S$ 256.05525, found 256.05563; IR (ATR, cm^{-1}): *ν*=2948 (w), 2205 (w), 1716 (m), 1694 (s), 1598 (w), 1568 (w), 1525 (m), 1483 (m), 1454 (w), 1434 (m), 1409 (m), 1376 (m), 1298 (m), 1283 (m), 1232 (s), 1200 (w), 1188 (w), 1158 (w), 1096 (m), 1074 (s), 1001 (m), 938 (m), 878 (w), 848 (m), 819 (w), 754 (s).

6.36. Methyl 3-((4-propylphenyl)ethynyl)thiophene-2-carboxylate (4d)

Yellow oil, yield 0.207 g, 73%. ^1H NMR (300 MHz, $CDCl_3$): *δ*=0.86 (t, *J*=7.4 Hz, 3H, Me), 1.57 (sext, *J*=7.6 Hz, 2H, CH_2), 2.52 (t, *J*=7.8 Hz, 2H, CH_2), 3.85 (s, 3H, MeO), 7.09 (d, *J*=8.4 Hz, 2H), 7.11 (d, *J*=5.2 Hz, 1H), 7.37 (d, *J*=5.1 Hz, 1H), 7.42 (d, *J*=8.3 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): *δ*=12.7, 23.2, 36.9, 51.1, 82.3, 94.6, 119.0, 127.5, 129.3, 130.2, 130.7, 131.0, 131.9, 142.7, 160.8; GC–MS (EI, 70 eV): *m*/*z* (%)=284 (M^+, 83), 269 (11), 255 (100), 240 (33), 184 (9), 170 (8), 152 (10), 139 (8); HRMS (ESI): calcd for $C_{17}H_{16}O_2S$ 284.00866, found 284.00868; IR (ATR, cm^{-1}): *ν*=2953 (m), 2208 (m), 1697 (s), 1605 (w), 1530 (m), 1503 (m), 1434 (s), 1410 (m), 1379 (m), 1353 (w), 1297 (m), 1232 (s), 1188 (w), 1095 (m), 1074 (s), 1019 (w), 1001 (w), 968 (w), 939 (m), 878 (m), 839 (m), 813 (w), 790 (w), 770 (s).

6.37. Methyl 3-((4-*tert*-butylphenyl)ethynyl)thiophene-2-carboxylate (4e)

Yellow oil, yield 0.210 g, 70%. ^1H NMR (300 MHz, $CDCl_3$): *δ*=1.25 (s, 9H, 3Me), 3.86 (s, 3H, MeO), 7.12 (d, *J*=5.1 Hz, 1H), 7.30 (d, *J*=8.6 Hz, 2H), 7.38 (d, *J*=5.1 Hz, 1H), 7.44 (d, *J*=8.6 Hz, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): *δ*=31.1, 34.8, 83.3, 95.5, 117.1, 119.8, 125.3, 127.2, 131.5, 132.1, 133.1, 133.5, 152.0, 161.9; GC–MS (EI, 70 eV): *m*/*z* (%)= 298 (M^+, 45), 283 (100), 251 (16), 240 (6), 179 (7), 139 (6), 112 (12); HRMS (ESI): calcd for $C_{18}H_{18}O_2S$ 298.10220, found 298.10236; IR (ATR, cm^{-1}): *ν*=3106 (w), 2954 (m), 2210 (w), 1922 (w), 1805 (w), 1702 (s), 1650 (w), 1573 (w), 1528 (m), 1503 (m), 1463 (w), 1434 (s),

1409 (m), 1374 (m), 1365 (m), 1354 (w), 1288 (m), 1241 (s), 1188 (w), 1157 (w), 1117 (w), 1099 (m), 1073 (m), 1024 (w), 1015 (w), 970 (w), 905 (w), 879 (m), 846 (w), 830 (m), 784 (s).

6.38. Methyl 3-((4-methoxyphenyl)ethynyl)thiophene-2-carboxylate (4f)

Yellow oil, yield 0.192 g, 70%. ^{1}H NMR (250 MHz, $CDCl_3$): δ=3.72 (s, 3H, MeO), 3.83 (s, 3H, MeO), 6.78 (d, J=8.9 Hz, 2H), 7.08 (d, J=5.1 Hz, 1H), 7.35 (d, J=5.1 Hz, 1H), 7.43 (d, J=8.9 Hz, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=52.1, 55.2, 82.9, 95.6, 114.0, 114.9, 127.8, 130.4, 131.9, 132.6, 133.3, 160.0, 161.9; GC–MS (EI, 70 eV): m/z (%)=272 (M^+, 100), 257 (68), 241 (14), 229 (12), 214 (9), 201 (8), 186 (7), 169 (20), 158 (6), 144 (5), 126 (7); HRMS (ESI): calcd for $C_{15}H_{12}O_3S$ 272.05012, found 272.05037; IR (ATR, cm^{-1}): ν=3112 (w), 2953 (w), 2204 (w), 1702 (s), 1650 (w), 1601 (m), 1566 (w), 1526 (m), 1503 (m), 1466 (w), 1452 (w), 1434 (s), 1410 (m), 1373 (m), 1292 (m), 1240 (s), 1179 (m), 1170 (m), 1100 (m), 1073 (m), 1023 (m), 935 (w), 905 (w), 931 (s), 783 (s).

6.39. Methyl 3-((4-fluorophenyl)ethynyl)thiophene-2-carboxylate (4g)

Yellow oil, yield 0.195 g, 75%. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.82 (s, 3H, MeO), 6.92–6.98 (m, 2H), 7.09 (d, J=5.1 Hz, 1H), 7.36 (d, J=5.2 Hz, 1H), 7.44–7.49 (m, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=52.1, 83.7, 94.2, 115.7 (d, J=22.1 Hz), 119.0 (d, J=3.5 Hz), 127.3, 130.5, 131.9, 133.3, 133.7 (d, J=8.5 Hz), 161.7, 162.8 (d, J=250.2 Hz); ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−110.0 (s, CF); GC–MS (EI, 70 eV): m/z (%)=260 (M^+, 100), 245 (74), 229 (38), 217 (31), 202 (6), 189 (14), 157 (56), 131 (9), 114 (6), 100 (5); HRMS (ESI): calcd for $C_{14}H_9FO_2S$ 260.03018, found 260.03069; IR (ATR, cm^{-1}): ν=3081 (m), 2949 (w), 2214 (w), 1711 (s), 1673 (w), 1644 (w), 1633 (w), 1599 (m), 1524 (m), 1501 (s), 1469 (w), 1454 (w), 1433 (s), 1409 (m), 1383 (m), 1303 (s), 1219 (s), 1189 (w), 1156 (m), 1102 (m), 1092 (w), 1080 (s), 1015 (w), 1005 (w), 939 (m), 848 (w), 831 (s), 770 (s).

6.40. Methyl 3-(pent-1-ynyl)thiophene-2-carboxylate (4h)

Yellow oil, yield 0.104 g, 50%. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.00 (t, J=7.4 Hz, 3H, Me), 1.59 (sext, J=7.4 Hz, 2H, CH_2), 2.39 (t, J=7.0 Hz, 2H, CH_2), 3.81 (s, 3H, MeO), 7.00 (d, J=5.1 Hz, 1H), 7.32 (d, J=5.1 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=13.5, 21.7, 22.0, 52.0, 75.3, 97.1, 117.1, 128.4, 130.1, 132.5, 161.9; GC–MS (EI, 70 eV): m/z (%)=208 (M^+, 6), 193 (14), 180 (100), 165 (18), 161 (9), 149 (18), 137 (11), 120 (8), 108 (8), 93 (7); HRMS (ESI): calcd for $C_{11}H_{12}O_2S$ 208.05525, found 208.05515; IR (ATR, cm^{-1}): ν=2955 (m), 2229 (w), 1717 (s), 1697 (s), 1524 (m), 1505 (m), 1434 (s), 1410 (s), 1377 (m), 1352 (w), 1337 (w), 1268 (m), 1242 (m), 1221 (s), 1188 (w), 1158 (w), 1072 (s), 1022 (w), 998 (w), 962 (w), 933 (w), 877 (m), 847 (w), 766 (s).

6.41. Methyl 3-(hex-1-ynyl)thiophene-2-carboxylate (4i)

Yellow oil, yield 0.115 g, 51%. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.82 (t, J=7.2 Hz, 3H, Me), 1.29–1.45 (m, 4H, $2CH_2$), 2.17 (t, J=7.1 Hz, 2H, CH_2), 3.82 (s, 3H, MeO), 7.01 (d, J=5.1 Hz, 1H), 7.39 (d, J=5.1 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=13.4, 18.8, 21.8, 30.3, 52.1, 97.2, 117.1, 130.1, 131.2, 132.4, 132.9, 161.1; GC–MS (EI, 70 eV): m/z (%)=222 (M^+, 9), 207 (4), 193 (11), 180 (100), 165 (24), 161 (18), 149 (12), 137 (17), 121 (10), 108 (8), 93 (5); HRMS (ESI): calcd for $C_{12}H_{14}O_2S$ 222.07090, found 222.07135; IR (ATR, cm^{-1}): ν=2955 (m), 2231 (w), 1723 (s), 1525 (w), 1506 (m), 1456 (w), 1435 (s), 1411 (s), 1378 (m), 1353 (m), 1317 (w), 1284 (w), 1243 (s), 1189 (w), 1158 (w), 1077 (s), 968 (w), 932 (w), 878 (m), 851 (w), 819 (w), 767 (s).

6.42. Methyl 3-(hept-1-ynyl)thiophene-2-carboxylate (4j)

Yellow oil, yield 0.131 g, 55%. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.85 (t, J=7.2 Hz, 3H, Me), 1.26–1.41 (m, 4H, $2CH_2$), 1.58 (quint, J=7.6 Hz, 2H, CH_2), 2.40 (t, J=7.1 Hz, 2H, CH_2), 3.83 (s, MeO), 7.02 (d, J=5.2 Hz, 1H), 7.39 (d, J=5.2 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=13.9, 19.7, 22.2, 28.2, 29.6, 31.1, 52.2, 117.1, 130.1, 131.2, 132.5, 132.9, 161.2; GC–MS (EI, 70 eV): m/z (%)=236 (M^+, 20), 204 (13), 193 (14), 189 (14), 180 (100), 175 (21), 165 (28), 149 (16), 137 (21), 121 (12), 108 (11), 93 (7); HRMS (ESI): calcd for $C_{13}H_{16}O_2S$ 236.08655, found 236.08722; IR (ATR, cm^{-1}): ν=2929 (m), 2228 (w), 1720 (s), 1525 (w), 1505 (m), 1434 (s), 1411 (s), 1377 (m), 1352 (m), 1269 (m), 1241 (s), 1189 (w), 1158 (w), 1072 (s), 967 (w), 930 (w), 877 (s), 818 (w), 765 (s).

6.43. 3-(Phenylethynyl)thiophene-2-carboxamide (5a)

White solid, yield 0.080 g, 86%, mp 145–147 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=6.46 (s, 2H, NH_2), 7.13 (d, J=5.1 Hz, 1H), 7.29–7.35 (m, 3H), 7.41 (d, J=5.1 Hz, 1H), 7.44–7.47 (m, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=83.2, 96.3, 121.3, 121.5, 128.6, 129.4, 129.9, 131.6, 131.7, 140.4, 163.1; GC–MS (EI, 70 eV): m/z (%)=227 (M^+, 100), 211 (19), 198 (14), 171 (18), 139 (37), 113 (8); HRMS (ESI): calcd for $C_{13}H_9NOS$ 227.03994, found 227.03968; IR (ATR, cm^{-1}): ν=3428 (m), 3131 (m), 2957 (w), 2208 (w), 1950 (w), 1656 (s), 1599 (s), 1518 (w), 1503 (w), 1485 (m), 1469 (w), 1417 (s), 1397 (m), 1350 (m), 1279 (w), 1238 (w), 1170 (m), 1158 (w), 1127 (m), 1103 (w), 1070 (m), 1048 (w), 1029 (m), 1010 (w), 978 (m), 915 (m), 880 (m), 847 (m), 780 (m), 750 (s), 686 (s).

6.44. 3-(*p*-Tolylethynyl)thiophene-2-carboxamide (5b)

White solid, yield 0.085 g, 88%, mp 143–144 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.31 (s, 3H, Me), 6.51 (s, 2H, NH_2), 6.98 (d, J=5.3 Hz, 1H), 7.12 (d, J=7.8 Hz, 2H), 7.35 (d, J=8.1 Hz, 2H), 7.41 (d, J=5.3 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=21.6, 82.7, 96.7, 110.0, 118.4, 121.6, 129.4, 129.9, 131.5, 131.7, 139.9, 163.3; GC–MS (EI, 70 eV): m/z (%)=241 (M^+, 100), 226 (17), 212 (21), 198 (5), 185 (5), 171 (8), 112 (5); HRMS (ESI): calcd for $C_{14}H_{11}NOS$ 241.05559, found 241.05621; IR (ATR, cm^{-1}): ν=3439 (m), 3143 (m), 2201 (w), 1651 (s), 1594 (s), 1524 (w), 1501 (m), 1462 (w), 1425 (s), 1372 (m), 1349 (m), 1309 (w), 1275 (w), 1240 (w), 1211 (w), 1185 (m), 1160 (w), 1106 (m), 1089 (w), 1044 (w), 975 (m), 877 (m), 817 (s), 774 (s), 709 (s).

6.45. 3-(*o*-Tolylethynyl)thiophene-2-carboxamide (5c)

White solid, yield 0.080 g, 85%, mp 136–137 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.43 (s, 3H, Me), 6.24 (s, 2H, NH_2), 7.11–7.26 (m, 4H), 7.41–7.43 (m, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=20.8, 86.9, 95.4, 121.3, 121.6, 125.9, 129.5, 129.8, 130.0, 131.8, 132.1, 140.0, 140.2, 163.0; GC–MS (EI, 70 eV): m/z (%)=241 (M^+, 12), 224 (100), 212 (33), 195 (28), 184 (5), 171 (6), 152 (26), 136 (12), 112 (7), 98 (6); HRMS (ESI): calcd for $C_{14}H_{11}NOS$ (M+H) 242.00634, found 242.06315; IR (ATR, cm^{-1}): ν=3423 (s), 3132 (m), 2202 (w), 1657 (s), 1600 (s), 1557 (w), 1538 (w), 1516 (w), 1483 (m), 1450 (m), 1416 (s), 1394 (m), 1349 (m), 1292 (w), 1271 (w), 1174 (w), 1162 (w), 1129 (m), 1100 (m), 1073 (w), 1045 (w), 981 (m), 943 (m), 891 (w), 867 (w), 851 (m), 775 (s), 748 (s), 714 (s).

6.46. 3-((4-Propylphenyl)ethynyl)thiophene-2-carboxamide (5d)

White solid, yield 0.085 g, 90%, mp 158–159 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.87 (t, J=7.4 Hz, 3H, Me), 1.58 (sext, J=7.5 Hz, 2H, CH_2), 2.55 (t, J=7.9 Hz, 2H, CH_2), 5.95 (s, 2H, NH_2), 7.12 (d, J=5.2 Hz, 1H), 7.13 (d, J=8.1 Hz, 2H), 7.37 (d, J=8.2 Hz, 2H), 7.41 (d,

J=5.1 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=13.7, 24.2, 37.9, 82.7, 96.6, 118.6, 121.6, 128.8, 129.9, 131.5, 131.6, 140.1, 144.6, 162.9; GC–MS (EI, 70 eV): m/z (%)=269 (M^+, 60), 240 (100), 212 (10), 196 (5), 184 (5), 170 (5), 152 (8), 139 (5); HRMS (ESI): calcd for $C_{16}H_{15}NOS$ 269.08689, found 269.08756; IR (ATR, cm^{-1}): ν=3385 (m), 3154 (m), 2926 (m), 2209 (w), 1632 (s), 1608 (s), 1526 (m), 1497 (m), 1436 (s), 1398 (m), 1353 (m), 1278 (w), 1205 (w), 1186 (w), 1167 (w), 1124 (m), 1087 (m), 1072 (w), 1018 (m), 978 (s), 949 (w), 886 (w), 843 (m), 790 (s), 725 (s).

6.47. 3-((4-*tert*-Butylphenyl)ethynyl)thiophene-2-carboxamide (5e)

White solid, yield 0.079 g, 84%, mp 179–181 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.25 (s, 9H, 3Me), 6.41 (s, 2H, NH_2), 7.12 (d, J=5.1 Hz, 1H), 7.33 (d, J=8.7 Hz, 2H), 7.39 (d, J=5.1 Hz, 1H), 7.39 (d, J=8.6 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=30.0, 33.9, 81.7, 95.6, 117.4, 120.5, 124.6, 128.8, 130.3, 130.6, 139.2, 152.0, 162.1; GC–MS (EI, 70 eV): m/z (%)=283 (M^+, 52), 268 (100), 251 (9), 240 (5), 179 (6), 112 (11); HRMS (ESI): calcd for $C_{17}H_{17}NOS$ 283.10254, found 283.10272; IR (ATR, cm^{-1}): ν=3443 (m), 3115 (m), 2954 (m), 1658 (s), 1601 (s), 1552 (w), 1524 (w), 1497 (w), 1462 (w), 1426 (m), 1397 (m), 1362 (m), 1349 (m), 1265 (m), 1197 (w), 1170 (w), 1108 (m), 1072 (w), 1016 (m), 981 (m), 946 (w), 850 (w), 834 (s), 777 (s).

6.48. 3-((4-Methoxyphenyl)ethynyl)thiophene-2-carboxamide (5f)

White solid, yield 0.077 g, 81%, mp 188–189 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.77 (s, 3H, MeO), 6.21 (s, 2H, NH_2), 6.84 (d, J=8.7 Hz, 2H), 7.11 (d, J=5.1 Hz, 1H), 7.39 (d, J=8.8 Hz, 2H), 7.40 (d, J=5.1 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=55.3, 82.2, 96.6, 113.5, 114.3, 121.7, 129.9, 131.6, 133.1, 134.5, 160.5, 163.0; GC–MS (EI, 70 eV): m/z (%)=257 (M^+, 100), 242 (82), 214 (15), 186 (10), 169 (12), 154 (5), 144 (5), 136 (5), 126 (5), 115 (6); HRMS (ESI): calcd for $C_{14}H_{11}NO_2S$ (M+H) 258.05833, found 258.05846; IR (ATR, cm^{-1}): ν=3425 (m), 3130 (m), 2201 (m), 1657 (s), 1600 (s), 1567 (w), 1558 (w), 1521 (m), 1500 (m), 1453 (w), 1417 (m), 1397 (m), 1348 (m), 1306 (w), 1293 (m), 1254 (m), 1180 (m), 1149 (w), 1126 (w), 1110 (m), 1070 (w), 1029 (m), 976 (m), 955 (w), 939 (w), 895 (w), 831 (s), 771 (s).

6.49. 3-((4-Fluorophenyl)ethynyl)thiophene-2-carboxamide (5g)

White solid, yield 0.076 g, 80%, mp 161–162 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=6.40 (s, 2H, NH_2), 6.99–7.05 (m, 2H), 7.12 (d, J=5.1 Hz, 1H), 7.42 (d, J=5.2 Hz, 1H), 7.44–7.47 (m, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=83.0, 95.2, 116.0 (d, J=22.2 Hz), 117.6 (d, J=3.6 Hz), 121.1, 130.0, 131.7, 133.6 (d, J=8.6 Hz), 140.4, 163.0, 163.1 (d, J=251.8 Hz); ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−108.6 (s, CF); IR (ATR, cm^{-1}): ν=3429 (m), 3130 (m), 2210 (w), 1893 (w), 1657 (s), 1597 (s), 1556 (w), 1519 (m), 1499 (m), 1469 (w), 1424 (s), 1398 (m), 1349 (m), 1296 (w), 1276 (w), 1220 (m), 1172 (w), 1154 (m), 1127 (w), 1091 (m), 1072 (w), 1014 (m), 979 (m), 957 (w), 943 (w), 880 (w), 849 (m), 932 (s).

6.50. 3-(Pent-1-ynyl)thiophene-2-carboxamide (5h)

Colorless oil, yield 0.080 g, 86%. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.98 (t, J=7.4 Hz, 3H, Me), 1.59 (sext, J=7.2 Hz, 2H, CH_2), 2.40 (t, J=7.1 Hz, 2H, CH_2), 6.33 (s, 2H, NH_2), 7.01 (d, J=5.1 Hz, 1H), 7.35 (d, J=5.1 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=13.6, 21.5, 21.9, 75.5, 98.4, 122.3, 129.4, 131.9, 139.6, 163.6; GC–MS (EI, 70 eV): m/z (%)=193 (M^+, 3), 178 (15), 165 (100), 147 (4), 136 (14), 120 (6), 109 (6), 93 (5); HRMS (ESI): calcd for $C_{10}H_{11}NOS$ (M+H) 194.06341, found 194.06375; IR (ATR, cm^{-1}): ν=3456 (s), 3136 (s), 1656 (s), 1597 (s), 1501 (m), 1462 (w), 1423 (s), 1371 (m), 1350 (m), 1275 (w), 1239 (w), 1159 (w), 1131 (w), 1112 (m), 1089 (m), 1060 (w), 1014 (w), 908 (w), 875 (w), 823 (w), 767 (s), 708 (s).

6.51. 3-(Hex-1-ynyl)thiophene-2-carboxamide (5i)

Colorless oil, yield 0.075 g, 80%. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.88 (t, J=7.2 Hz, 3H, Me), 1.35 (m, 2H, CH_2), 1.65 (quint, J=7.8 Hz, 2H, CH_2), 2.41 (t, J=7.1 Hz, 2H, CH_2), 6.66 (s, 2H, NH_2), 7.00 (d, J=5.1 Hz, 1H), 7.34 (d, J=5.1 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=13.5, 19.2, 22.0, 30.4, 98.5, 122.3, 129.6, 131.9, 139.6, 163.5; GC–MS (EI, 70 eV): m/z (%)=207 (M^+, 17), 192 (5), 178 (24), 165 (100), 147 (6), 136 (22), 121 (7), 109 (7), 93 (6); HRMS (ESI): calcd for $C_{11}H_{13}NOS$ 207.07124, found 207.07147; IR (ATR, cm^{-1}): ν=3430 (m), 3159 (m), 2929 (m), 2223 (m), 1652 (s), 1596 (s), 1519 (w), 1455 (w), 1419 (s), 1393 (m), 1348 (m), 1323 (w), 1298 (w), 1239 (w), 1209 (w), 1186 (w), 1132 (w), 1105 (w), 1071 (w), 1050 (w), 1035 (w), 992 (w), 978 (w), 959 (w), 928 (w), 898 (m), 770 (s), 711 (s).

6.52. 3-(Hept-1-ynyl)thiophene-2-carboxamide (5j)

Colorless oil, yield 0.076 g, 81%. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.83 (t, J=7.2 Hz, 3H, Me), 1.24–1.37 (m, 4H, $2CH_2$), 1.54 (quint, J=7.6 Hz, 2H, CH_2), 2.40 (t, J=7.2 Hz, 2H, CH_2), 6.67 (s, 2H, NH_2), 7.00 (d, J=5.1 Hz, 1H), 7.34 (d, J=5.1 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=12.9, 18.5, 21.1, 27.0, 28.6, 30.1, 74.3, 97.5, 121.2, 128.6, 130.9, 138.6, 162.5; GC–MS (EI, 70 eV): m/z (%)=221 (M^+, 28), 206 (5), 192 (10), 178 (39), 165 (100), 152 (7), 141 (8), 136 (25), 120 (9), 109 (9), 93 (6); HRMS (ESI): calcd for $C_{12}H_{15}NOS$ (M+H) 222.09471, found 222.09427; IR (ATR, cm^{-1}): ν=3431 (m), 3153 (m), 2926 (s), 2223 (w), 1657 (s), 1597 (s), 1538 (w), 1519 (w), 1455 (w), 1421 (s), 1394 (m), 1347 (m), 1325 (w), 1241 (w), 1110 (w), 1071 (w), 1052 (w), 1022 (w), 975 (w), 889 (w), 862 (w), 770 (s), 707 (s).

6.53. 5-Phenylthieno[2,3-*c*]pyridin-7(6*H*)-one (6a)

White solid, yield 0.075 g, 75%, mp 169–170 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=6.88 (s, 1H), 7.21 (d, J=5.2 Hz, 1H), 7.39–7.47 (m, 3H), 7.64–7.67 (m, 2H), 7.67 (d, J=5.2 Hz, 1H), 10.53 (s, 1H, NH); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=100.6, 123.6, 125.3, 127.3, 128.2, 128.5, 132.9, 133.1, 140.6, 146.0, 159.0; GC–MS (EI, 70 eV): m/z (%)=227 (M^+, 100), 198 (4), 171 (12), 149 (6), 121 (3), 95 (5); HRMS (ESI): calcd for $C_{13}H_9NOS$ 227.03994, found 227.04038; IR (ATR, cm^{-1}): ν=3143 (w), 2917 (w), 1650 (s), 1613 (w), 1600 (w), 1576 (w), 1558 (w), 1538 (w), 1525 (w), 1498 (s), 1448 (w), 1425 (w), 1355 (w), 1307 (w), 1259 (m), 1207 (w), 1185 (m), 1157 (w), 1131 (m), 1095 (w), 1078 (w), 1053 (m), 1029 (w), 967 (w), 920 (w), 905 (w), 879 (m), 832 (m), 810 (s), 759 (s).

6.54. 5-*p*-Tolylthieno[2,3-*c*]pyridin-7(6*H*)-one (6b)

White solid, yield 0.077 g, 77%, mp 254–255 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.35 (s, 3H, Me), 6.85 (s, 1H), 7.18–7.25 (m, 3H), 7.49 (d, J=8.1 Hz, 2H), 7.68 (d, J=5.1 Hz, 1H), 9.72 (s, 1H, NH); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=21.2, 101.2, 124.7, 126.0, 130.1, 131.2, 134.1, 135.3, 137.1, 139.9, 141.4, 147.2; GC–MS (EI, 70 eV): m/z (%)=241 (M^+, 100), 226 (3), 212 (3), 197 (2), 184 (3), 171 (4), 149 (4), 121 (3), 95 (4); HRMS (ESI): calcd for $C_{14}H_{11}NOS$ (M+H) 242.06341, found 242.06378; IR (ATR, cm^{-1}): ν=3135 (w), 2914 (w), 1625 (s), 1613 (m), 1568 (w), 1511 (m), 1471 (m), 1453 (w), 1303 (w), 1280 (w), 1185 (m), 1153 (w), 1131 (m), 1109 (w), 1057 (w), 1043 (m), 1020 (w), 935 (w), 892 (m), 852 (m), 830 (m), 805 (s).

6.55. 5-*o*-Tolylthieno[2,3-*c*]pyridin-7(6*H*)-one (6c)

White solid, yield 0.077 g, 77%, mp 160–161 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.31 (s, 3H, Me), 6.59 (s, 1H), 7.21–7.31 (m,

5H), 7.70 (d, *J*=5.2 Hz, 1H), 9.49 (s, 1H, NH); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=20.0, 29.6, 104.0, 124.5, 126.2, 129.3, 129.6, 130.9, 134.1, 134.3, 136.0, 141.4, 146.8, 159.2; GC–MS (EI, 70 eV): *m*/*z* (%)=241 (M^+, 100), 222 (16), 212 (4), 195 (3), 184 (4), 152 (4), 95 (5); HRMS (ESI): calcd for $C_{14}H_{11}NOS$ (M+H) 242.06341, found 242.06299; IR (ATR, cm^{-1}): ν=3451 (w), 3255 (w), 3126 (w), 3017 (w), 2920 (w), 2851 (w), 1608 (s), 1557 (m), 1524 (w), 1487 (w), 1454 (w), 1403 (w), 1370 (w), 1307 (w), 1292 (w), 1276 (w), 1261 (w), 1159 (w), 1131 (m), 1106 (m), 1039 (m), 939 (w), 880 (m), 859 (w), 830 (m), 756 (s), 715 (s).

6.56. 5-(4-Propylphenyl)thieno[2,3-*c*]pyridin-7(6*H*)-one (6d)

White solid, yield 0.072 g, 72%, mp 198–199 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.90 (t, *J*=7.4 Hz, 3H, Me), 1.61 (sext, *J*=7.3 Hz, 2H, CH_2), 2.58 (t, *J*=7.9 Hz, 2H, CH_2), 6.86 (s, 1H), 7.19 (d, *J*=5.2 Hz, 1H), 7.24 (d, *J*=8.3 Hz, 2H), 7.58 (d, *J*=8.3 Hz, 2H), 7.66 (d, *J*=5.2 Hz, 1H), 10.74 (s, 1H, NH); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=13.8, 24.3, 37.7, 101.2, 124.6, 126.2, 127.9, 129.3, 131.4, 133.9, 141.8, 144.5, 147.2, 160.1; GC–MS (EI, 70 eV): *m*/*z* (%)=269 (M^+, 71), 240 (100), 225 (2), 210 (3), 184 (4), 152 (2); HRMS (ESI): calcd for $C_{16}H_{15}NOS$ 269.08689, found 269.08749; IR (ATR, cm^{-1}): ν=3260 (w), 2951 (w), 2866 (w), 1622 (s), 1601 (m), 1564 (w), 1539 (w), 1514 (m), 1464 (w), 1455 (w), 1433 (w), 1423 (w), 1395 (w), 1349 (w), 1306 (w), 1294 (w), 1273 (w), 1187 (m), 1131 (m), 1107 (w), 964 (w), 949 (w), 884 (m), 834 (w), 796 (s).

6.57. 5-(4-*tert*-Butylphenyl)thieno[2,3-*c*]pyridin-7(6*H*)-one (6e)

White solid, yield 0.070 g, 70%, mp 246–247 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.25 (s, 9H, 3Me), 6.87 (s, 1H), 7.21 (d, *J*=5.2 Hz, 1H), 7.45 (d, *J*=8.6 Hz, 2H), 7.58 (d, *J*=8.6 Hz, 2H), 7.67 (d, *J*=5.1 Hz, 1H), 10.26 (s, 1H, NH); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=31.2, 34.8, 101.3, 124.7, 125.9, 126.3, 131.1, 131.3, 134.0, 141.5, 147.2, 153.0, 159.9; GC–MS (EI, 70 eV): *m*/*z* (%)=283 (M^+, 65), 268 (100), 252 (4), 240 (12), 210 (3), 120 (11); HRMS (ESI): calcd for $C_{17}H_{17}NOS$ (M+H) 284.11036, found 284.10983; IR (ATR, cm^{-1}): ν=3261 (w), 3139 (w), 3040 (w), 2958 (m), 2865 (w), 1626 (s), 1605 (m), 1562 (w), 1537 (w), 1517 (m), 1461 (m), 1423 (w), 1392 (w), 1361 (m), 1305 (w), 1266 (m), 1201 (w), 1126 (m), 1058 (w), 1042 (m), 1016 (w), 950 (w), 906 (m), 887 (m), 839 (m), 817 (s).

6.58. 5-(4-Methoxyphenyl)thieno[2,3-*c*]pyridin-7(6*H*)-one (6f)

White solid, yield 0.076 g, 76%, mp 141–142 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ=3.81 (s, 3H, MeO), 6.87 (s, 1H), 6.96 (d, *J*=8.9 Hz, 2H), 7.22 (d, *J*=5.2 Hz, 1H), 7.58 (d, *J*=6.8 Hz, 2H), 7.71 (d, *J*=5.2 Hz, 1H), 10.31 (s, 1H, NH); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=55.4, 101.4, 114.8, 124.6, 126.2, 127.5, 134.5, 141.3, 141.5, 147.6, 159.6, 160.9; GC–MS (EI, 70 eV): *m*/*z* (%)=257 (M^+, 100), 242 (24), 214 (21), 187 (5), 128 (3), 115 (7), 95 (4); HRMS (ESI): calcd for $C_{14}H_{11}NO_2S$ 257.05050, found 257.05104; IR (ATR, cm^{-1}): ν=3255 (w), 3129 (w), 3071 (w), 2831 (w), 1620 (m), 1604 (s), 1556 (w), 1530 (w), 1514 (s), 1468 (w), 1454 (w), 1435 (w), 1394 (w) 1360 (w), 1313 (w), 1287 (m), 1248 (s), 1202 (w), 1179 (m), 1133 (m), 1062 (w), 1044 (m), 937 (w), 921 (w), 882 (m), 856 (m), 812 (s).

6.59. 5-(4-Fluorophenyl)thieno[2,3-*c*]pyridin-7(6*H*)-one (6g)

White solid, yield 0.075 g, 75%, mp 279–280 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.03 (s, 1H), 7.32–7.37 (m, 2H), 7.42 (d, *J*=5.1 Hz, 1H), 7.79–7.84 (m, 2H), 8.08 (d, *J*=5.1 Hz, 1H), 11.76 (s, 1H, NH); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=100.9, 115.6 (d, *J*=21.7 Hz), 125.2, 127.8, 129.2 (d, *J*=8.6 Hz), 130.4 (d, *J*=3.1 Hz), 134.3, 140.9, 146.3, 158.9, 162.6 (d, *J*=246.8 Hz); ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−112.3 (s, CF); GC–MS (EI, 70 eV): *m*/*z* (%)=245 (M^+, 100), 218 (6), 189 (14), 172 (2), 149 (6), 122 (4), 95 (10); HRMS (ESI): calcd for $C_{13}H_8FOS$ 245.03051, found 245.03040; IR (ATR, cm^{-1}): ν=3271 (w), 3146 (w), 3043 (w), 1650 (s), 1615 (m), 1557 (w), 1526 (w), 1506 (s), 1455 (w), 1434 (w), 1424 (w), 1394 (w), 1372 (w), 1360 (w), 1307 (w), 1276 (m), 1221 (s), 1160 (s), 1133 (m), 1107 (m), 1048 (s), 1014 (w), 937 (w), 911 (m), 888 (m), 833 (s).

6.60. 5-Propylthieno[2,3-*c*]pyridin-7(6*H*)-one (6h)

White solid, yield 0.075 g, 75%, mp 95–96 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.93 (t, *J*=7.4 Hz, 3H, Me), 1.70 (sext, *J*=7.3 Hz, 2H, CH_2), 2.60 (t, *J*=7.7 Hz, 2H, CH_2), 6.42 (s, 1H), 7.09 (d, *J*=5.2 Hz, 1H), 7.60 (d, *J*=5.2 Hz, 1H), 11.99 (s, 1H, NH); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=13.5, 22.0, 35.0, 101.5, 124.1, 126.8, 133.3, 144.2, 147.4, 161.1; GC–MS (EI, 70 eV): *m*/*z* (%)=193 (M^+, 66), 178 (22), 165 (100), 151 (4), 137 (46), 122 (7), 109 (14), 95 (12), 69 (8); HRMS (ESI): calcd for $C_{10}H_{11}NOS$ 193.05559, found 193.05534; IR (ATR, cm^{-1}): ν=3130 (w), 3059 (w), 2957 (w), 2866 (w), 2800 (w), 1632 (s), 1557 (w), 1524 (m), 1471 (m), 1453 (m), 1427 (w), 1377 (m), 1313 (w), 1228 (w), 1165 (m), 1129 (m), 1077 (m), 1048 (s), 995 (w), 911 (m), 858 (w), 830 (m), 807 (m), 784 (m).

6.61. 5-Butylthieno[2,3-*c*]pyridin-7(6*H*)-one (6i)

White solid, yield 0.073 g, 73%, mp 114–115 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.83 (t, *J*=7.3 Hz, 3H, Me), 1.35 (m, 2H, CH_2), 1.65 (quint, *J*=7.8 Hz, 2H, CH_2), 2.61 (t, *J*=7.8 Hz, 2H, CH_2), 6.46 (s, 1H), 7.11 (d, *J*=5.1 Hz, 1H), 7.64 (d, *J*=5.1 Hz, 1H), 11.32 (s, 1H, NH); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=13.7, 22.1, 30.8, 30.9, 32.9, 101.9, 124.1, 133.8, 144.0, 147.6, 160.5; GC–MS (EI, 70 eV): *m*/*z* (%)=207 (M^+, 47), 192 (4), 178 (11), 165 (100), 137 (24), 122 (8), 109 (7), 95 (8); HRMS (ESI): calcd for $C_{11}H_{13}NOS$ 207.07124, found 207.07176; IR (ATR, cm^{-1}): ν=3454 (w), 3267 (w), 2957 (m), 2930 (m), 2860 (m), 1615 (s), 1552 (w), 1528 (m), 1463 (m), 1427 (m), 1372 (m), 1326 (w), 1302 (w), 1281 (w), 1259 (w), 1227 (w), 1211 (w), 1167 (m), 1124 (w), 1101 (w), 1087 (m), 1047 (m), 1016 (w), 981 (w), 894 (m), 848 (m), 835 (m), 773 (s), 722 (s).

6.62. 5-Pentylthieno[2,3-*c*]pyridin-7(6*H*)-one (6j)

White solid, yield 0.070 g, 70%, mp 142–143 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.83 (t, *J*=7.1 Hz, 3H, Me), 1.28–1.33 (m, 4H, $2CH_2$), 1.67 (quint, *J*=7.6 Hz, 2H, CH_2), 2.60 (t, *J*=7.8 Hz, 2H, CH_2), 6.42 (s, 1H), 7.09 (d, *J*=5.2 Hz, 1H), 7.60 (d, *J*=5.1 Hz, 1H), 11.62 (s, 1H, NH); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=13.9, 22.3, 28.4, 31.1, 33.2, 101.4, 124.1, 133.4, 133.7, 144.3, 147.4, 160.9; GC–MS (EI, 70 eV): *m*/*z* (%)=221 (M^+, 45), 192 (6), 178 (21), 165 (100), 137 (23), 122 (6), 109 (6), 95 (5); HRMS (ESI): calcd for $C_{12}H_{15}NOS$ (M+H) 222.09471, found 222.09495; IR (ATR, cm^{-1}): ν=3128 (w), 2951 (m), 2853 (m), 1645 (w), 1621 (s), 1529 (m), 1470 (m), 1435 (m), 1386 (w), 1372 (w), 1340 (w), 1316 (w), 1300 (w), 1267 (w), 1241 (w), 1226 (w), 1200 (w), 1169 (m), 1105 (w), 1091 (m), 1049 (m), 1007 (w), 986 (w), 962 (w), 912 (m), 859 (m), 835 (m), 774 (m), 722 (s).

6.63. 2-(Phenylethynyl)-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile (7a)

Yellow solid, yield 77%, mp 79–80 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.75–1.80 (m, 4H, $2CH_2$), 2.58–2.66 (m, 4H, $2CH_2$), 7.18–7.29 (m, 3H), 7.46–7.49 (m, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=20.8, 21.8, 23.4, 23.9, 79.0, 98.6, 113.2, 113.4, 120.9, 127.4, 128.2, 128.4, 130.6, 135.3, 137.7; GC–MS (EI, 70 eV): *m*/*z* (%)=263 (M^+, 100), 235 (75), 190 (8), 145 (5); HRMS (ESI): calcd for $C_{17}H_{13}NS$ (M+H) 264.08410, found 264.08450; IR (ATR, cm^{-1}): ν=2923 (s),

2215 (s), 1939 (w), 1596 (w), 1540 (m), 1494 (w), 1436 (m), 1403 (m), 1349 (w), 1337 (w), 1298 (m), 1260 (w), 1185 (w), 1144 (w), 1109 (m), 1067 (m), 1026 (m), 951 (w), 916 (m), 880 (m), 942 (w), 745 (s), 682 (s).

6.64. 2-(*p*-Tolylethynyl)-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile (7b)

Yellow solid, yield 77%, mp 110–112 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.74–1.80 (m, 4H, $2CH_2$), 2.29 (s, 3H, Me), 2.58–2.65 (m, 4H, $2CH_2$), 7.09 (d, J=7.9 Hz, 2H), 7.36 (d, J=8.1 Hz, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=21.6, 21.8, 22.8, 24.4, 24.9, 100.0, 114.1, 114.3, 118.8, 129.2, 129.8, 131.1, 136.2, 138.4, 13.9.5; GC–MS (EI, 70 eV): m/z (%)=277 (M^+, 100), 249 (62), 233 (5), 190 (5); HRMS (ESI): calcd for $C_{18}H_{15}NS$ 277.09197, found 277.09204; IR (ATR, cm^{-1}): ν=2931 (s), 2223 (s), 1547 (m), 1512 (w), 1504 (w), 1445 (m), 1403 (w), 1348 (w), 1294 (m), 1259 (w), 1240 (w), 1178 (w), 1141 (w), 1104 (m), 1077 (w), 1041 (w), 1017 (w), 949 (w), 900 (w), 880 (m), 844 (w), 813 (s).

6.65. 2-((4-Propylphenyl)ethynyl)-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile (7c)

Yellow solid, yield 73%, mp 58–59 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.85 (t, J=7.4 Hz, 2H, CH_2), 1.56 (sext, J=7.3 Hz, 2H, CH_2), 1.75–1.79 (m, 4H, $2CH_2$), 2.53 (t, J=7.3 Hz, 3H, Me), 2.57–2.64 (m, 4H, $2CH_2$), 7.08 (d, J=8.2 Hz, 2H), 7.38 (d, J=8.2 Hz, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=13.7, 21.8, 22.8, 24.2, 24.4, 24.9, 38.0, 79.5, 100.1, 114.1, 114.3, 119.0, 128.6, 129.8, 131.6, 136.2, 138.4, 144.3; GC–MS (EI, 70 eV): m/z (%)=305 (M^+, 94), 276 (100), 260 (5), 248 (23); HRMS (ESI): calcd for $C_{20}H_{19}NS$ 305.12327, found 305.12307; IR (ATR, cm^{-1}): ν=2930 (s), 2221 (s), 1604 (w), 1546 (m), 1513 (w), 1459 (m), 1434 (m), 1401 (w), 1348 (w), 1338 (w), 1293 (m), 1258 (w), 1240 (w), 1188 (w), 1178 (w), 1136 (w), 1104 (m), 1053 (w), 1030 (w), 985 (w), 950 (w), 903 (w), 880 (m), 809 (s).

6.66. 2-((4-*tert*-Butylphenyl)ethynyl)-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile (7d)

Yellow solid, yield 73%, mp 132–134 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.25 (s, 9H, 3Me), 1.75–1.80 (m, 4H, $2CH_2$), 2.58–2.66 (m, 4H, $2CH_2$), 7.30 (d, J=8.6 Hz, 2H), 7.41 (d, J=8.6 Hz, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=21.8, 22.8, 24.4, 24.9, 31.1, 34.9, 79.5, 100.0, 114.1, 114.3, 118.8, 125.4, 129.8, 131.4, 136.2, 138.3, 152.6; GC–MS (EI, 70 eV): m/z (%)=319 (M^+, 57), 304 (100), 276 (14), 261 (5), 235 (5), 138 (5), 124 (10); HRMS (ESI): calcd for $C_{21}H_{21}NS$ 319.13892, found 319.13931; IR (ATR, cm^{-1}): ν=2944 (s), 2218 (s), 1909 (w), 1790 (w), 1660 (w), 1603 (w), 1545 (m), 1505 (w), 1456 (m), 1435 (m), 1403 (m), 1361 (m), 1346 (w), 1334 (w), 1294 (m), 1264 (m), 1200 (w), 1135 (w), 1115 (m), 1095 (m), 1013 (m), 950 (m), 899 (w), 878 (m), 831 (s).

6.67. 2-((4-Methoxyphenyl)ethynyl)-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile (7e)

Yellow solid, yield 75%, mp 88–90 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.75–1.78 (m, 4H, $2CH_2$), 2.58–2.65 (m, 4H, $2CH_2$), 3.75 (s, 3H, MeO), 6.80 (d, J=8.9 Hz, 2H), 7.41 (d, J=8.9 Hz, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=21.8, 22.8, 24.4, 24.9, 55.3, 79.0, 100.0, 113.8, 113.9, 114.1, 114.4, 133.3, 134.0, 136.1, 138.1, 160.3; GC–MS (EI, 70 eV): m/z (%)=293 (M^+, 100), 278 (12), 265 (37), 250 (9), 222 (7); HRMS (ESI): calcd for $C_{18}H_{15}NOS$ 293.08689, found 293.08751; IR (ATR, cm^{-1}): ν=2950 (m), 2839 (m), 2217 (s), 1600 (s), 1563 (w), 1547 (m), 1504 (m), 1454 (m), 1439 (m), 1416 (w), 1347 (w), 1334 (w), 1317 (w), 1287 (m), 1249 (s), 1182 (w), 1167 (m), 1103 (m), 1076 (w), 1025 (s), 962 (w), 951 (w), 941 (w), 829 (s).

6.68. 2-(*o*-Tolylethynyl)-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile (7f)

Yellow solid, yield 78%, mp 88–89 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.75–1.81 (m, 4H, $2CH_2$), 2.45 (s, 3H, Me), 2.59–2.67 (m, 4H, $2CH_2$), 7.07–7.22 (m, 3H), 7.43 (d, J=7.5 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=19.7, 20.8, 21.8, 23.4, 23.9, 82.8, 97.7, 113.2, 113.3, 120.7, 124.6, 128.2, 128.6, 128.7, 130.8, 135.3, 137.5, 139.5; GC–MS (EI, 70 eV): m/z (%)=277 (M^+, 100), 262 (5), 249 (40), 221 (5), 216 (6), 189 (5), 115 (7); HRMS (ESI): calcd for $C_{18}H_{15}NS$ 277.09197, found 277.09155; IR (ATR, cm^{-1}): ν=2917 (m), 2216 (s), 1549 (m), 1494 (w), 1461 (m), 1434 (m), 1402 (w), 1375 (w), 1347 (w), 1336 (w), 1295 (m), 1198 (w), 1181 (w), 1155 (w), 1138 (w), 1093 (m), 1029 (m), 986 (w), 951 (w), 882 (m), 865 (w), 846 (w), 761 (s).

6.69. 2-((4-Fluorophenyl)ethynyl)-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile (7g)

Yellow solid, yield 75%, mp 89–91 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.75–1.80 (m, 4H, $2CH_2$), 2.58–2.66 (m, 4H, $2CH_2$), 6.95–7.01 (m, 2H), 7.44–7.48 (m, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=21.8, 22.8, 24.4, 24.9, 79.7, 98.5, 114.2, 114.4, 115.8 (d, J=22.3 Hz), 118.0 (d, J=3.6 Hz), 129.2, 133.7 (d, J=8.5 Hz), 136.3, 138.8, 163.0 (d, J=251.4 Hz); ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=–109.0 (s, CF); GC–MS (EI, 70 eV): m/z (%)=281 (M^+, 100), 253 (83), 240 (5), 208 (8), 163 (7); HRMS (ESI): calcd for $C_{17}H_{12}FNS$ 281.06690, found 281.06701; IR (ATR, cm^{-1}): ν=2908 (m), 2221 (s), 1899 (w), 1598 (s), 1546 (m), 1509 (s), 1456 (m), 1433 (m), 1348 (w), 1335 (w), 1294 (w), 1259 (w), 1233 (s), 1153 (s), 1093 (m), 1025 (w), 985 (w), 950 (w), 879 (m), 833 (s).

6.70. 2-(Phenylethynyl)-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxamide (8a)

White solid, yield 75%, mp 178–179 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.69–1.78 (m, 4H, $2CH_2$), 2.64–2.69 (m, 2H, CH_2), 2.79–2.83 (m, 2H, CH_2), 5.75 (s, NH_2), 7.28–7.32 (m, 3H), 7.40–7.44 (m, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=22.3, 22.8, 25.3, 26.2, 82.0, 98.8, 120.2, 122.0, 128.5, 129.1, 131.3, 136.5, 137.0, 138.8, 165.8; GC–MS (EI, 70 eV): m/z (%)=281 (M^+, 100), 266 (20), 253 (11), 234 (5), 225 (6), 202 (6), 176 (6), 105 (6); HRMS (ESI): calcd for $C_{17}H_{15}NOS$ 281.08689, found 281.08649; IR (ATR, cm^{-1}): ν=3373 (m), 3173 (m), 2932 (m), 1639 (s), 1613 (m), 1573 (w), 1546 (w), 1494 (w), 1470 (m), 1433 (m), 1368 (m), 1331 (w), 1294 (m), 1254 (w), 1180 (w), 1165 (w), 1124 (w), 1097 (w), 1070 (w), 1025 (w), 997 (w), 987 (w), 953 (w), 914 (m), 883 (m), 839 (m), 751 (s).

6.71. 2-(*p*-Tolylethynyl)-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxamide (8b)

White solid, yield 77%, mp 209–210 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.68–1.78 (m, 4H, $2CH_2$), 2.30 (s, 3H, Me), 2.64–2.68 (m, 2H, CH_2), 2.79–2.83 (m, 2H, CH_2), 5.78 (s, 2H, NH_2), 7.10 (d, J=7.9 Hz, 2H), 7.31 (d, J=8.1 Hz, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=21.5, 22.4, 22.8, 25.3, 26.2, 81.4, 99.2, 118.9, 120.6, 129.3, 131.2, 136.1, 137.0, 138.5, 139.4, 165.1; GC–MS (EI, 70 eV): m/z (%)=295 (M^+, 100), 280 (18), 267 (8), 252 (5), 239 (6), 203 (7), 176 (5), 139 (5), 119 (9); HRMS (ESI): calcd for $C_{18}H_{17}NOS$ 295.10254, found 295.10273; IR (ATR, cm^{-1}): ν=3374 (m), 3198 (m), 2921 (m), 1635 (s), 1614 (m), 1546 (w), 1512 (w), 1469 (m), 1431 (m), 1366 (m), 1333 (w), 1294 (w), 1251 (w), 1179 (w), 1162 (w), 1106 (m), 1068 (w), 1021 (w), 952 (w), 941 (w), 878 (w), 833 (w), 812 (s).

6.72. 2-((4-Propylphenyl)ethynyl)-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxamide (8c)

White solid, yield 79%, mp 175–177 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.86 (t, J=7.4 Hz, 3H, Me), 1.57 (sext, J=7.4 Hz, 2H, CH_2), 1.68–1.78 (m, 4H, $2CH_2$), 2.53 (q, J=7.3 Hz, 2H, CH_2), 2.64–2.68 (m, 2H, CH_2), 2.80–2.84 (m, 2H, CH_2), 7.10 (d, J=8.3 Hz, 2H), 7.33 (d, J=8.3 Hz, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=13.6, 22.4, 22.8, 24.2, 25.3, 26.2, 37.9, 81.4, 99.3, 119.1, 120.6, 128.7, 131.2, 136.1, 137.0, 138.5, 144.2, 165.1; GC–MS (EI, 70 eV): m/z (%)=323 (M^+, 100), 308 (15), 294 (20), 266 (7), 203 (8), 175 (5), 147 (7); HRMS (ESI): calcd for $C_{20}H_{21}NOS$ 323.13384, found 323.13322; IR (ATR, cm^{-1}): ν=3367 (m), 3176 (m), 2926 (m), 1637 (s), 1613 (s), 1546 (w), 1513 (w), 1463 (m), 1433 (m), 1368 (m), 1334 (w), 1295 (m), 1251 (w), 1242 (w), 1178 (w), 1164 (w), 1095 (m), 1017 (w), 950 (w), 878 (w), 837 (m), 809 (m).

6.73. 2-((4-*tert*-Butylphenyl)ethynyl)-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxamide (8d)

White solid, yield 74%, mp 149–150 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.25 (s, 9H, 3Me), 1.72–1.75 (m, 4H, $2CH_2$), 2.60–2.66 (m, 2H, CH_2), 2.80–2.82 (m, 2H, CH_2), 5.74 (s, 2H, NH_2), 7.31 (d, J=8.7 Hz, 2H), 7.36 (d, J=8.7 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=22.4, 22.8, 25.4, 26.3, 31.1, 34.9, 81.4, 99.2, 118.9, 120.6, 125.5, 131.1, 136.2, 137.0, 138.5, 152.6, 165.2; GC–MS (EI, 70 eV): m/z (%)=337 (M^+, 100), 322 (30), 304 (11), 294 (5), 280 (5), 203 (6), 147 (6); HRMS (ESI): calcd for $C_{21}H_{23}NOS$ (M+H) 338.15731, found 338.15713; IR (ATR, cm^{-1}): ν=3452 (m), 3154 (m), 2925 (m), 1665 (s), 1596 (m), 1537 (w), 1504 (w), 1454 (m), 1415 (m), 1360 (m), 1291 (m), 1265 (w), 1250 (m), 1193 (w), 1163 (w), 1112 (m), 1087 (w), 1025 (w), 1015 (w), 956 (w), 878 (w), 830 (s).

6.74. 2-((4-Methoxyphenyl)ethynyl)-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxamide (8e)

White solid, yield 77%, mp 212–214 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.72–1.77 (m, 4H, $2CH_2$), 2.64–2.67 (m, 2H, CH_2), 2.80–2.83 (m, 2H, CH_2), 3.76 (s, 3H, MeO), 5.67 (s, 2H, NH_2), 6.81 (d, J=8.9 Hz, 2H), 7.36 (d, J=8.9 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=22.4, 22.8, 25.3, 26.3, 55.3, 80.8, 99.2, 114.0, 114.2, 120.8, 132.9, 135.9, 137.0, 138.2, 160.3, 165.2; GC–MS (EI, 70 eV): m/z (%)=311 (M^+, 100), 296 (18), 283 (11), 268 (11), 156 (4), 121 (4); HRMS (ESI): calcd for $C_{18}H_{17}NO_2S$ (M+H) 312.10528, found 312.10501; IR (ATR, cm^{-1}): ν=3387 (m), 3177 (m), 2932 (m), 2540 (w), 2203 (w), 1617 (m), 1601 (s), 1558 (w), 1543 (w), 1512 (m), 1462 (m), 1431 (m), 1369 (w), 1331 (w), 1291 (m), 1249 (s), 1172 (m), 1161 (m), 1098 (m), 1022 (m), 952 (w), 877 (w), 827 (s).

6.75. 2-(*o*-Tolylethynyl)-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxamide (8f)

White solid, yield 79%, mp 169–170 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.68–1.80 (m, 4H, $2CH_2$), 2.39 (s, 3H, Me), 2.65–2.69 (m, 2H, CH_2), 2.79–2.83 (m, 2H, CH_2), 5.83 (s, 2H, NH_2), 7.08–7.23 (m, 3H), 7.38 (d, J=7.5 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=20.7, 22.3, 22.8, 25.3, 26.2, 85.5, 98.1, 120.6, 121.8, 125.7, 128.4, 129.1, 129.7, 131.7, 135.9, 137.0, 138.7, 140.0; GC–MS (EI, 70 eV): m/z (%)=295 (M^+, 100), 278 (48), 267 (10), 250 (16), 234 (12), 221 (10), 202 (10), 178 (8), 165 (8), 139 (10), 119 (10), 115 (9); HRMS (ESI): calcd for $C_{18}H_{17}NOS$ 295.10254, found 295.10150; IR (ATR, cm^{-1}): ν=3363 (m), 3173 (m), 2930 (m), 1635 (s), 1614 (m), 1547 (w), 1494 (w), 1468 (m), 1434 (m), 1368 (m), 1333 (w), 1294 (m), 1272 (w), 1252 (w), 1180 (w), 1166 (w), 1120 (m), 1040 (m), 951 (w), 939 (w), 879 (w), 817 (w), 803 (w), 749 (s).

6.76. 2-((4-Fluorophenyl)ethynyl)-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxamide (8g)

White solid, yield 72%, mp 170–172 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.69–1.78 (m, 4H, $2CH_2$), 2.64–2.68 (m, 2H, CH_2), 2.78–2.82 (m, 2H, CH_2), 5.86 (s, 2H, NH_2), 6.96–7.02 (m, 2H), 7.38–7.43 (m, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=22.3, 22.8, 25.3, 26.1, 81.7, 97.6, 115.9 (d, J=22.3 Hz), 118.2 (d, J=3.6 Hz), 119.9, 133.3 (d, J=8.6 Hz), 136.6, 136.9, 138.9, 163.0 (d, J=250.9 Hz), 165.1; ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−109.2 (s, CF); GC–MS (EI, 70 eV): m/z (%)=299 (M^+, 100), 284 (21), 271 (11), 243 (7), 220 (6), 183 (5), 176 (6), 163 (5), 123 (9); HRMS (ESI): calcd for $C_{17}H_{14}FNOS$ 299.07746, found 299.07765; IR (ATR, cm^{-1}): ν=3362 (m), 3174 (m), 2932 (m), 1638 (s), 1615 (m), 1598 (m), 1546 (w), 1510 (m), 1468 (m), 1434 (m), 1368 (w), 1334 (w), 1294 (w), 1226 (s), 1180 (w), 1153 (m), 1093 (m), 1012 (w), 951 (w), 879 (w), 830 (s).

6.77. 3-Phenyl-6,7,8,9-tetrahydro[1]benzothieno[3,2-*c*]pyridin-1(2*H*)-one (9a)

White solid, yield 78%, mp 238–240 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.75–1.84 (m, 4H, $2CH_2$), 2.72–2.75 (m, 2H, CH_2), 3.07–3.08 (m, 2H, CH_2), 6.86 (s, 1H), 7.32–7.43 (m, 3H), 7.67–7.71 (m, 2H), 10.97 (s, 1H, NH); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=22.3, 23.0, 25.4, 26.0, 100.5, 126.2, 128.4, 129.1, 129.3, 133.8, 134.0, 135.1, 139.5, 148.4, 160.9; GC–MS (EI, 70 eV): m/z (%)=281 (M^+, 100), 266 (5), 253 (29), 225 (9), 210 (3), 190 (4), 165 (3), 152 (2), 140 (3), 117 (2), 90 (4); HRMS (ESI): calcd for $C_{17}H_{15}NOS$ 281.08689, found 281.08734; IR (ATR, cm^{-1}): ν=3137 (w), 3074 (w), 3022 (w), 2928 (m), 2847 (w), 1688 (m), 1633 (s), 1594 (m), 1551 (m), 1504 (m), 1443 (m), 1403 (w), 1361 (w), 1334 (w), 1286 (m), 1230 (m), 1178 (w), 1159 (w), 1147 (w), 1137 (w), 1066 (w), 1035 (w), 994 (m), 966 (w), 948 (w), 912 (m), 829 (m), 756 (s).

6.78. 3-*p*-Tolyl-6,7,8,9-tetrahydro[1]benzothieno[3,2-*c*]pyridin-1(2*H*)-one (9b)

White solid, yield 77%, mp 254–256 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.80–1.82 (m, 4H, $2CH_2$), 2.34 (s, 3H, Me), 2.72–2.74 (m, 2H, CH_2), 3.06–3.08 (m, 2H, CH_2), 6.86 (s, 1H), 7.21 (d, J=8.2 Hz, 2H), 7.54 (d, J=8.2 Hz, 2H), 10.51 (s, 1H, NH); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=24.8, 26.1, 26.8, 29.2, 29.7, 104.7, 129.9, 130.7, 133.7, 134.7, 137.4, 139.2, 143.6, 143.7, 153.0, 164.9; GC–MS (EI, 70 eV): m/z (%)=295 (M^+, 100), 280 (6), 267 (21), 252 (6), 239 (6), 190 (4), 148 (3), 133 (2); HRMS (ESI): calcd for $C_{18}H_{17}NOS$ (M+H) 296.11036, found 296.11088; IR (ATR, cm^{-1}): ν=3364 (w), 3138 (w), 3077 (w), 3011 (w), 2915 (m), 2837 (w), 2728 (w), 1687 (m), 1635 (s), 1599 (m), 1564 (w), 1552 (w), 1519 (m), 1445 (w), 1424 (w), 1399 (w), 1360 (w), 1335 (w), 1321 (w), 1286 (m), 1247 (m), 1196 (w), 1171 (w), 1128 (m), 1068 (w), 1038 (w), 993 (m), 965 (w), 937 (w), 881 (m), 837 (w), 817 (m), 786 (s).

6.79. 3-(4-Propylphenyl)-6,7,8,9-tetrahydro[1]benzothieno[3,2-*c*]pyridin-1(2*H*)-one (9c)

White solid, yield 80%, mp 228–230 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.89 (t, J=7.4 Hz, 3H, Me), 1.60 (sext, J=7.4 Hz, 2H, CH_2), 1.79–1.81 (m, 4H, $2CH_2$), 2.57 (t, J=7.7 Hz, 2H, CH_2), 2.73 (m, 2H, CH_2), 3.07 (m, 2H, CH_2), 6.82 (s, 1H), 7.20 (d, J=8.3 Hz, 2H), 7.60 (d, J=8.3 Hz, 2H), 11.07 (s, 1H, NH); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=13.7, 22.4, 23.1, 24.3, 25.4, 26.0, 37.7, 100.0, 126.2, 127.1, 129.1, 131.3, 134.0, 134.6, 139.9, 144.1, 148.5, 161.1; GC–MS (EI, 70 eV): m/z (%)=323 (M^+, 100), 308 (11), 294 (22), 281 (11), 265 (12), 249 (7), 233 (6), 207 (17), 186 (5), 148 (11); HRMS (ESI): calcd for $C_{20}H_{21}NOS$ 323.13384, found 323.13353; IR (ATR, cm^{-1}): ν=3359 (w), 3255 (w), 3138 (w), 3077 (w), 3013 (w), 2925 (m), 2852 (w), 1683 (w), 1632

(s), 1595 (m), 1557 (m), 1517 (m), 1462 (w), 1454 (w), 1434 (m), 1417 (w), 1402 (m), 1376 (w), 1333 (m), 1287 (m), 1247 (m), 1195 (w), 1170 (w), 1125 (m), 1093 (w), 1035 (w), 991 (m), 952 (w), 885 (m), 829 (m), 787 (s).

6.80. 3-(4-*tert*-Butylphenyl)-6,7,8,9-tetrahydro[1]benzothieno[3,2-*c*]pyridin-1(2*H*)-one (9d)

White solid, yield 79%, mp 283–285 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.28 (s, 9H, 3Me), 1.75–1.83 (m, 4H, $2CH_2$), 2.71–2.77 (m, 2H, CH_2), 3.06–3.09 (m, 2H, CH_2), 6.81 (s, 1H), 7.43 (d, J=8.7 Hz, 2H), 7.55 (d, J=8.7 Hz, 2H), 10.20 (s, 1H, NH); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=22.3, 23.0, 25.4, 26.0, 31.2, 34.7, 100.3, 125.7, 126.2, 130.8, 134.0, 134.3, 135.0, 139.4, 148.6, 152.8, 160.9; IR (ATR, cm^{-1}): ν=3075 (w), 2931 (m), 2826 (w), 2778 (w), 2715 (w), 2682 (w), 1682 (w), 1622 (s), 1600 (s), 1516 (m), 1462 (w), 1454 (w), 1442 (w), 1427 (w), 1384 (w), 1361 (s), 1268 (m), 1202 (w), 1170 (w), 1134 (w), 1111 (w), 1066 (w), 1018 (w), 993 (m), 967 (m), 902 (m), 824 (w), 838 (s), 801 (s), 773 (s).

6.81. 3-(4-Methoxyphenyl)-6,7,8,9-tetrahydro[1]benzothieno[3,2-*c*]pyridin-1(2*H*)-one (9e)

White solid, yield 73%, mp 265–268 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.80–1.84 (m, 4H, $2CH_2$), 2.72–2.76 (m, 2H, CH_2), 3.04–3.08 (m, 2H, CH_2), 3.8 (s, 3H, CH_3), 6.82 (s, 1H), 6.92 (d, J=8.6 Hz, 2H), 7.60 (d, J=8.6 Hz, 2H), 10.67 (s, 1H, NH); GC–MS (EI, 70 eV): m/z (%)=311 (M^+, 100), 296 (17), 283 (28), 268 (3), 231 (3), 181 (6), 169 (5), 131 (8), 119 (8); HRMS (ESI): calcd for $C_{18}H_{17}NO_2S$ 311.09745, found 311.09732; IR (ATR, cm^{-1}): ν=3271 (w), 3134 (w), 3077 (w), 2928 (m), 2832 (w), 1633 (s), 1606 (m), 1567 (m), 1515 (s), 1470 (w), 1451 (m), 1423 (w), 1398 (w), 1361 (w), 1339 (w), 1317 (w), 1285 (m), 1243 (s), 1178 (m), 1138 (m), 1118 (m), 1064 (w), 1028 (m), 993 (m), 938 (w), 879 (m), 851 (w), 806 (s).

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