

Convenient synthesis of thieno[3,2-*b*]indoles and thieno[3,4*b*]indoles by sequential site-selective Suzuki- and double C-N coupling reaction

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Abstract: A convenient synthesis of thieno[3,2-*b*]indoles and thieno[3,4-*b*]indoles has been developed. The protocol involves a site-selective Suzuki reaction, followed by a double C-N coupling reaction using anilines, benzylamines as well as alkylamines. The yields range from good to excellent.

Keywords: catalysis; cyclizations; cross-coupling reactions; regioselectivity; heterocycles

Introduction

Thiophene is a five-membered heterocycle which occurs on earth mostly as a minority in petroleum. Despite this minority, thiophene possesses a great potential for application in many fields of daily life. In pharmacology, thiophene is considered as a bioisostere of benzene.¹ Thus, replacing benzene by a thiophene moiety, scientists have discovered better alternatives for previously known drugs.² For instance, Olanzapine has been applied as a thiophene-analog of Clozapine for the treatment of schizophrenia with lower risk of side effects (Fig. 1).³ In biological research, thiophenes may incorporated into structures of fluorescent markers for cell labeling, such as compound DTTO (Fig. 1).⁴ Finally, in material science, thiophene is integrated in various organic electronic structures with low oxidation potential and environmental stability.⁵ Among these polymers, those involving fused thiophenes belong to the most studied classes, since they represent promising candidates for OFET applications. For example, DTTQ (Fig. 1), which is a fused thiophene-quinoxaline based polymer, possesses increased photochemical stability.⁶

In this regard, two fused derivatives comprised of thiophene and indole, namely thieno[3,2-*b*]indoles and thieno[3,4-*b*]indoles, have been considered to represent potential candidates for various applications. Former derivatives are known to possess antiviral properties.⁷ They also can be employed as building blocks of polymers for solar cell applications. For example, TI-DTBT3 (Fig. 1) is a donor-acceptor conjugated polymer which displays relatively high charge carrier mobility.⁸ As a result, the development of their syntheses has attracted increasing attention from synthetic chemists.





Figure 1: Relevant thiophene-related compounds

The first syntheses of thieno[3,2-*b*]indole and thieno[3,4-*b*]indole were carried out in 1982 by treating (a) substituted indole with thioamide⁹ and (b) 3-hydroxythiophene with hydrazine¹⁰ (Scheme 1). Unfortunately, these syntheses are not modular, thus not enabling a pathway to a large product library. Until 2000, there was no further report with respect to the enhancement of the synthetic elaboration of these two classes. Fortunately, the access to these thienoindoles has been facilitated during the last two decades owing to the development of palladium cross-coupling chemistry. With the high potential for creating new C-C and C-N bonds by palladium catalysts, a number of new synthetic methods for these classes have been developed. Generally, these protocols start with a Suzuki reaction to construct the C-C bond between the thiophene and the benzene ring, followed by different types of ring closures, such as (c) nitrene insertion,¹¹ (d) oxidative C-N coupling¹² or (e) Cadogan cyclisation¹³ to furnish the desired products (Scheme 1).



Scheme 1: Previously reported synthesis of thieno[3,2-b]indole and thieno[3,4-b]indole



Scheme 2: Retrosynthesis of thieno[3,2-b]indole and thieno[3,4-b]indole in this study

In an attempt to synthesize thieno[3,2-*b*]indoles and thieno[3,4-*b*]indoles, we also disconnected these molecules first by a Suzuki reaction (Scheme 2). However, we chose (2-bromophenyl)boronic acid to generate a biaryl derivative which is capable of undergoing a subsequent double C-N coupling. This strategy has proven effective in our previous studies related to the preparation of different fused indols.¹⁴ In this paper, we present our results for the synthesis of thieno[3,2-*b*]indole and thieno[3,4-*b*]indole derivatives.

Results and discussion

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The synthesis of thieno[3,2-*b*]indoles was initiated by a site-selective Suzuki reaction of 2,3-dibromothiophene (1) adapting our previously documented conditions for the preparation of diindolothiophene.^{14b} Under these conditions, 3-bromo-2-(2-bromophenyl) thiophene (2) was obtained in 82% yield (Scheme 3).



Scheme 3: Selective Suzuki reaction of 2,3-dibromothiophene

Subsequently, 3-bromo-2-(2-bromophenyl) thiophene (**2**) was employed as precursor for the double C-N coupling. To optimize this reaction, a brief ligand screening was conducted using the base NaO*t*Bu in toluene with the palladium source Pd_2dba_3 .^{14b, 15} During the optimization, the bidentate ligand dppf performed most effectively, generating **3a** in excellent 97% yield (Table 1).

Table 1	1 : O	ptimization	for s	ynthesis	of thieno	[3,2-b	indole 3a
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^a The yields were referred to as isolated yields.

With these optimized conditions in hand, the scope for the double C-N coupling was examined. In this regard, 15 different electron-rich amines were applied, giving corresponding thienoindoles **3a-o** in good to excellent yields (Table 2). For electron-poor,

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benzylic and aliphatic amines, application of dppf as ligand gave low yields of desired products. Thus, (*S*)-BINAP was employed as ligand, affording thienoindoles **3p-t** in very good yields (Table 2). Overall, the highest yield was obtained for the electron-rich system **3f** (98%), while the lowest occurred with the very large π -system **3o** (72%). The reaction proceeded effectively even with sterically encumbering amines, in case of **3b** and **3k** in 77% and 89% yield, respectively.

 Table 2: Synthesis of thieno[3,2-b]indoles 3a-t





^{*} $Pd_2dba_3 5 mol\%$, (S)-BINAP 5 mol%, NaOtBu 2.4 *equiv.*, toluene, 100 °C, 14h The yields were referred to as isolated yields.

Next, we turned our attention to the synthesis of thieno[3,4-*b*]indoles, which was obtained starting from 3,4-dibromothiophene (**4**). Using the same conditions applied for the Suzuki reaction of 2,3-dibromothiophene, 3-bromo-4-(2-bromophenyl)thiophene (**5**) was afforded selectively in 78% yield (Scheme 4).



Scheme 4: Selective Suzuki reaction of 3,4-dibromothiophene

Again, we tested several ligands for the double C-N coupling of **5**, under otherwise identical conditions. In this case, we became aware that the monodentate ligand $PtBu_3 \cdot HBF_4$ was most suitable for the reaction, giving thieno[3,4-*b*]indole **6a** in 95% yield (Table 3).

Br Br 5	+ H ₂ N 1.5 equiv.	Me N S 6a
Entry	Ligand [mol%]	Yield ^a
1	P <i>t</i> Bu₃·HBF₄ [10%]	95%
2	dppf [5%]	43%
3	SPhos [10%]	65%
4	(S)-BINAP [5%]	36%

Table 3: Optimization for the synthesis of thieno[3,4-b]indole 6a

^a The yields were referred to as isolated yields.

Using optimized conditions, we assessed the scope of the double C-N coupling. Noticeably, obtained yields for corresponding products were slightly lower than those for thieno[3,2-*b*]indoles **3a-t** (Table 4). The reason for this might refer to the lower stability of the thieno[3,2-*b*]indole derivatives.

Table 4: Synthesis of thieno[3,4-b]indole 6a-f





The yields were referred to as isolated yields.

Finally, we probed the feasibility of the method for the preparation of more structurally complex products, namely 5-substituted thieno[3,2-*b*]indoles. The synthesis started with two sequential site-selective Suzuki-reaction of 2,3,5-tribromothiophene (**7**) using our previously reported conditions.¹⁶ 2,3,5-tribromothiophene (**7**) was first converted to 2,3-dibromo-5-arylthiophenes **8a-d** and finally to the corresponding products **9a-d** (Table 5). Compared to the unsubstituted dibromothiophenes (Scheme 3 and 4), the yield of products obtained by the Suzuki reactions were remarkably lower in this case. It is most probably due to the presence of an additional aryl group at position 5 which might modulate the entire electronic nature of the molecule.

Table 5: Synthesis of 5-substituted preci	ursors 9a-d for double C-N coupling
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Br S Br	B(OH) ₂ R Pd(PPh ₃) ₄ 5 mol%, K ₂ CO ₃ , dioxane/toluene/water	R Ha K ₂ CO ₃ , 8a - 8d	D) ₂ B Br d(PPh ₃) ₄ 5 mol%, dioxane/toluene/water 9a - 9d
R		8 (% yield) ^a	9 (% yield) ^a
Н		a (60%)	a (43%)
CI		b (37%)	b (30%)
F		c (43%)	c (33%)
<i>t</i> Bu		d (43%)	d (26%)
<u>_</u>			

^a The yields were referred to as isolated yields.

With starting materials **9a-d** in hand, we tested different ligands for the double C-N coupling. In this case, Buchwald's biaryl ligand SPhos was most appropriate, furnishing corresponding thienoindole **10a** in 96% yield (Table 6).



Table 6: Optimization for the synthesis of 5-substituted thieno[3,2-b]indole 10a

^a The yields were referred to as isolated yields.

Applying optimized conditions, thienoindoles **10a-j** were prepared with moderate to excellent yield (Table 7). Evidently, the conditions can be applied for both electron-rich and electron-poor aryl amines, generating corresponding thienoindoles **10a-j** in the range of 45% to 95% yield. The highest yield was obtained for thienoindole **10a** (95%), while the lowest were obtained from thienoindoles **10i** and **10j** (both 45%). No clear correlation between the yields and chemical structures of 5-substituted thieno[3,2-*b*]indoles was observed.

Table 7: Synthesis of 5-substituted thieno[3,2-b]indoles 10a-j





The yields were referred to as isolated yields.

Conclusion

In conclusion, we developed a new synthetic pathway to thieno[3,2-*b*]indoles and thieno[3,4-*b*]indoles by site-selective Suzuki-reaction followed by double C-N coupling. In this protocol, electron-rich and electron-poor as well as aliphatic amines are compatible

nucleophiles. Despite the similarity of the starting materials, it became apparent that the choice of ligand is crucial for the final ring-closing double C-N coupling.

Experimental section

General information

If not otherwise stated, employed chemicals were obtained from commercial sources without further purifications. Chemicals used for work-up and purification were distilled prior usage. Column chromatography was carried out with silica gel with particle size between 0.006 and 0.043 mm. Product characterization was carried out using following devices. Melting point: Micro-Hot-Stage GalenTM III Cambridge Instrument.NMR: Bruker AVANCE 250 II, Bruker AVANCE 300 III and Bruker AVANCE 500 built 2006, 2007 and 2001, respectively.IR: Nicolet 380 FT-IR spectrometer using ATR sampling technique. GC/MS (EI, 70 eV): Finnigan MAT 95-XP device using HP-5 capillary column with helium carrier gas and electron ionization (EI) scan technique at 90 eV. HRMS: Finnigan MAT 95 XP device.

Melting point was carried out without further correction. For HRMS measurement, only signals with deviations of less than ±2 mDa were accounted as correct. NMR-peaks were calibrated using standard peaks of chloroform (7.260 ppm for ¹H, 72.160 ppm for ¹³C) and acetone (2.050 ppm for ¹H, 29.840 ppm for ¹³C). For peak descriptions, following abbreviations were used. NMR spectroscopy: s (singlet), d (doublet), t (triplet), dd (doublet doublet), dt (doublet triplet), td (triplet doublet), ddd (doublet doublet). IR spectroscopy: w (weak), m (medium), s (strong).

General procedure for the site-selective Suzuki reaction of 2,3-dibromothiophene and 3,4-dibromothiophene

2,3- or 3,4-Dibromothiophene (3 mmol), (2-bromophenyl)boronic acid (3.3 mmol), $Pd(PPh_3)_4$ (0.15 mmol), Na_2CO_3 (6 mmol) were added to a dried glass pressure tube. Next, the tube was evacuated and backfilled three times with argon. Afterwards, the solids were solved in 8 ml of 1,4-dioxane and 2 ml of distilled water. The tube was sealed by a Teflon cap and heated to 100 °C for 14 hours. After the reaction was finished (monitored by TLC), it was

10.1002/ejoc.201601281

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allowed to cool to room temperature and Na₂SO₄ was added to the mixture, diluted with ethyl acetate and filtered. The solvent was removed under reduced pressure. The crude oil was purified by column chromatography using heptane.

3-Bromo-2-(2-bromophenyl)thiophene (2): White solid, mp. 63 – 64 °C, 82% yield. ¹H NMR (500 MHz, Chloroform-*d*) δ = 7.69 (d, ³*J* = 8.0 Hz, 1H, CH_{Ar}), 7.42 – 7.34 (m, 3H, CH_{Ar}), 7.28 (ddd, ³*J* = 8.0 Hz, ³*J* = 6.7 Hz, ⁴*J* = 2.5 Hz, 1H, CH_{Ar}), 7.07 (d, ³*J* = 5.3 Hz, 1H, CH_{thiophene}). ¹³C NMR (126 MHz, CDCl₃) δ = 137.3 (C_{Ar}), 134.0 (C_{Ar}), 133.1 (CH_{Ar}), 132.9 (CH_{Ar}), 130.6 (CH_{Ar}), 130.3 (CH_{Ar}), 127.3 (CH_{Ar}), 126.2 (CH_{Ar}), 125.2 (C_{Ar}), 111.2 (C_{Ar}). IR (ATR, cm⁻¹): \tilde{v} = 3110 (w), 3085 (w), 3059 (w), 1528 (w), 1463 (m), 1419 (m), 1340 (m), 1148 (w), 1024 (m), 857 (m), 756 (s), 712 (s), 654 (m), 620 (m), 522 (m), 446 (m). MS (EI, 70 eV): *m/z* (%) = 318 [M]⁺ (45), 239 (22), 158 (100), 114 (30), 79 (21). HRMS (EI): Calculated for C₁₀H₆Br₂S [M]⁺ 315.85515 found 315.85464, calculated for C₁₀H₆Br⁸¹BrS [M]⁺ 317.85310 found 317.85281, calculated for C₁₀H₆⁸¹Br₂S [M]⁺ 319.85105 found 319.85069.

3-Bromo-4-(2-bromophenyl)thiophene (5): Colorless oil, 78% yield. ¹H NMR (500 MHz, Chloroform-*d*) $\delta = 7.67$ (d, ³*J* = 8.1 Hz, 1H_{Ar}), 7.39 – 7.34 (m, 2H, CH_{Ar}), 7.31 – 7.24 (m, 3H, CH_{Ar}). ¹³C NMR (126 MHz, CDCl₃) $\delta = 141.5$ (C_{Ar}), 136.6 (C_{Ar}), 132.9 (CH_{Ar}), 132.0 (CH_{Ar}), 129.8 (CH_{Ar}), 127.2 (CH_{Ar}), 124.9 (CH_{Ar}), 124.5 (C_{Ar}), 123.3 (CH_{Ar}), 112.4 (C_{Ar}). IR (ATR, cm⁻¹): $\tilde{v} = 3107$ (w), 3057 (w), 1560 (w), 1525 (w), 1464 (m), 1425 (m), 1339 (m), 1257 (w), 1081 (w), 1026 (m), 921 (m), 852 (m), 792 (m), 751 (s), 710 (m), 653 (m), 451 (m). MS (EI, 70 eV): *m/z* (%) = 320 (23), 318 [M]⁺ (43), 239 (31), 158 (100), 114 (26), 113 (20), 79 (24). HRMS (EI): Calculated for C₁₀H₆Br₂S [M]⁺ 315.85515 found 315.85490, calculated for C₁₀H₆Br⁸¹BrS [M]⁺ 317.85310 found 317.85301, calculated for C₁₀H₆⁸¹Br₂S [M]⁺ 319.85105 found 319.85073.

General procedure for the one-fold selective Suzuki reaction of 2,3,5-tribromothiophene

2,3,5-Tribromothiophene (10 mmol), arylboronic acid (11 mmol) and $Pd(PPh_3)_4$ (0.5 mmol) were dissolved in a mixture of 100 ml 1,4-dioxane/toluene (1:1) under argon atmosphere. To the reaction was added 40 ml aqueous 2M K₂CO₃. The reaction was heated to 80 °C for 8 hours. After the reaction was finished (monitored by TLC), it was allowed to cool to room temperature. The mixture was extracted with dichloromethane three times. The combined organic phases were collected and dried with Na₂SO₄, filtered and concentrated under vacuum. The residue was purified by column chromatography using heptane to obtain the pure product.

2,3-Dibromo-5-phenylthiophene (8a): White solid, mp. 68 – 69 °C, 60 % yield. ¹H NMR (250 MHz, Chloroform-*d*) δ = 7.53 – 7.45 (m, 2H, CH_{Ar}), 7.44 – 7.32 (m, 3H, CH_{Ar}), 7.10 (s, 1H, CH_{thiophene}). ¹³C NMR (63 MHz, CDCl₃) δ = 145.6 (C_{Ar}), 132.9 (C_{Ar}), 129.4 (2CH_{Ar}), 128.8 (CH_{Ar}), 125.8 (CH_{Ar}), 125.7 (2CH_{Ar}), 114.8 (C_{Ar}), 110.3 (C_{Ar}). IR (ATR, cm⁻¹): \tilde{v} = 3056 (w), 1579 (w), 1486 (m), 1446 (m), 1320 (w), 1292 (w), 1069 (w), 997 (m), 948 (w), 815 (s), 747 (s), 682 (s), 625 (w), 549 (w). MS (EI, 70 eV): *m/z* (%) = 320 [M⁺, ⁸¹Br] (43), 318 [M⁺] (88), 316 (41), 158 (58), 114 (12), 91 (14), 82 (18), 79 (26), 77 (5), 69 (10), 44 (15), 43 (9), 32 (100). HRMS (EI): Calculated for C₁₀H₆Br₂S [M]⁺ 315.85526 found 315.85515, calculated for C₁₀H₆Br⁸¹BrS [M]⁺ 317.85310 found 317.85326, calculated for C₁₀H₆⁸¹Br₂S [M]⁺ 319.85105 found 319,85119.

2,3-Dibromo-5-(4-chlorophenyl)thiophene (8b): White solid, mp. 104 – 105 °C, 37% yield. ¹H NMR (250 MHz, Chloroform-*d*) δ = 7.45 – 7.32 (m, 4H, CH_{Ar}), 7.08 (s, 1H, CH_{thiophene}). ¹³C NMR (63 MHz, CDCl₃) δ = 144.2 (C_{Ar}), 134.7 (C_{Ar}), 131.4 (C_{Ar}), 129.6 (2CH_{Ar}), 126.9 (2CH_{Ar}), 126.2 (CH_{thiophene}), 115.0 (C_{Ar}), 110.7 (C_{Ar}). IR (ATR, cm⁻¹): \tilde{v} = 3088 (w), 3033 (w), 1484 (m), 1429 (w), 1402 (w), 1318 (w), 1091 (m), 997 (w), 801 (s), 733 (w), 674 (m), 575 (w), 546 (w). MS (EI, 70 eV): *m*/*z* (%) = 356 (16), 355 (8), 354 [M⁺, ⁸¹Br] (72), 353 (12), 352 [M⁺] (100), 350 (43), 194 (17), 192 (46), 157 (11), 113 (15), 96 (8). HRMS (EI): Calculated for C₁₀H₅Br₂CIS [M]⁺ 349.81618 found 349.81584, calculated for C₁₀H₅Br⁸¹BrCIS 351.81413 found 351.81374, calculated for C₁₀H₅Br⁸¹Br³⁷CIS [M]⁺ 353.81118 found 353.81139, calculated for C₁₀H₅⁸¹Br₂CIS [M]⁺ 353.81208 found 353.81139, calculated for C₁₀H₅⁸¹Br₂³⁷CIS [M]⁺ 355.80913 found 355.80899.

2,3-Dibromo-5-(4-fluorophenyl)thiophene (8c): White solid, mp. 95 – 96 °C, 43% yield. ¹H NMR (300 MHz, Chloroform-*d*) δ = 7.44 (dd, ³*J* = 8.8 Hz, ³*J* = 5.1 Hz, 2H, CH_{Ar}), 7.08 (t, ³*J* = 8.6 Hz, 2H, CH_{Ar}), 7.02 (s, 1H, CH_{Ar}). ¹⁹F NMR (282.4 MHz, CDCl₃): δ = -112.5 (FC_{Ar}). ¹³C NMR (75 MHz, CDCl₃) δ = 163.1 (d, ¹*J*_{C-F} = 249.2 Hz, C_{Ar}), 144.4 (C_{Ar}), 129.2 (d, ⁴*J*_{C-F} = 3.4 Hz, FC_{Ar}), 127.5 (d, ³*J*_{C-F} = 8.2 Hz, 2CH_{Ar}), 125.8 (CH_{thiophene}), 116.4 (d, ²*J*_{C-F} = 22.0 Hz, 2CH_{Ar}), 114.8 (C_{Ar}), 110.2 (C_{Ar}). IR (ATR, cm⁻¹): \tilde{v} = 3089 (w), 1595 (w), 1494 (s), 1299 (m), 1232 (s), 1157 (m), 993 (m), 829 (s), 807 (s), 691 (m), 585 (m), 547 (m). MS (EI, 70 eV): *m/z* (%) = 336 [M]⁺ (100), 334 (48), 213 (6), 211 (6), 177 (8), 177 (76), 139 (6), 132 (20), 131 (13), 88 (11), 81 (7), 75 (6), 74 (4), 69 (6). HRMS (EI): Calculated for C₁₀H₅Br₂FS [M]⁺ 333.84573 found 333.84563, calculated for C₁₀H₅Br⁸¹BrFS [M]⁺ 335.84368 found 335.84353, calculated for C₁₀H₅⁸¹Br₂FS [M]⁺ 337.84163 found 337.84146.

2,3-Dibromo-5-(4-(*tert***-butyl)phenyl)thiophene (8d):** White solid, mp. 59 – 60 °C, 43% yield. ¹H NMR (300 MHz, Chloroform-*d*) δ = 7.42 (m, 4H, CH_{Ar}), 7.07 (s, 1H, CH_{thiophene}), 1.34 (s, 9H, *t*Bu). ¹³C NMR (75 MHz, CDCl₃) δ = 152.0 (C_{Ar}), 145.6 (C_{Ar}), 130.1 (C_{Ar}), 126.4

(2CH_{Ar}), 125.2 (2CH_{Ar}), 125.2 (CH_{thiophene}), 114.7 (C_{Ar}), 109.7 (C_{Ar}), 34.9 (C_{*t*Bu}), 31.4 (3CH₃). IR (ATR, cm⁻¹): \tilde{v} = 2958 (m), 2865 (w), 1496 (m), 1362 (m), 1267 (w), 1186 (w), 996 (m), 834 (m), 810 (s), 732 (m), 565 (s). MS (EI, 70 eV): *m/z* (%) = 376 (22), 374 [M⁺, ⁸¹Br] (42), 272 [M⁺] (21), 362 (7), 361 (52), 360 (15), 159 (100), 157 (50), 333 (9), 331 (16), 329 (8), 165 (10). HRMS (EI): Calculated for C₁₄H₁₄Br₂S [M]⁺ 371.91775, found 371.91695, calculated for C₁₄H₁₄Br⁸¹BrS [M]⁺ 373.91570, found 373.91505, calculated for C₁₄H₁₄⁸¹Br₂S [M]⁺ 375.91365, found 375.91293.

General procedure for the site-selective Suzuki reaction of 5-substituted 2,3dibromothiophene

5-Substituted 2,3-dibromothiophene (3 mmol), (2-bromophenyl)boronic acid (3.3 mmol) and $Pd(PPh_3)_4$ (0.15 mmol) were dissolved in 30 ml of mixture 1,4-dioxane/toluene (1:1) under argon atmosphere. To the reaction was added 12 ml aqueous 2M K₂CO₃. The reaction was heated to 80 °C for 12 hours (monitored by TLC). After cooling to room temperature, it was extracted with dichloromethane three times. The organic phases were collected and dried with Na₂SO₄, filtered and concentrated under reduced pressure. The crude oil was subjected to column chromatography using heptane to obtain the pure product.

3-Bromo-2-(2-bromophenyl)-5-phenylthiophene (9a): White solid, mp. 83 – 84 °C, 43% yield. ¹H NMR (250 MHz, Chloroform-*d*) δ = 7.70 (dd, ³*J* = 8.0 Hz, ⁴*J* = 1.3 Hz, 1H, CH_{Ar}), 7.62 – 7.53 (m, 2H, CH_{Ar}), 7.47 – 7.27 (m, 6H, CH_{Ar}), 7.25 (s, 1H, CH_{thiophene}). ¹³C NMR (63 MHz, CDCl₃) δ = 144.7 (C_{Ar}), 136.4 (C_{Ar}), 134.0 (CH_{Ar}), 133.3 (CH_{Ar}), 133.0 (C_{Ar}), 130.7 (CH_{Ar}), 129.3 (2CH_{Ar}), 128.5 (CH_{Ar}), 127.4 (CH_{Ar}), 126.0 (CH_{Ar}), 125.8 (2CH_{Ar}), 125.2 (C_{Ar}), 111.6 (C_{Ar}). IR (ATR, cm⁻¹): \tilde{v} = 3094 (w), 1538 (w), 1473 (m), 1447 (m), 1331 (w), 1073 (w), 1052 (w), 1027 (m), 823 (w), 757 (s), 749 (s), 722 (m), 688 (s), 649 (m), 572 (w). MS (EI, 70 eV): *m/z* (%) = 397 (9), 396 (53), 395 (18), 394 [M⁺] (100), 392 (51), 235 (14), 234 (69), 233 (14), 232 (10), 202 (16), 189 (29), 121 (17), 113 (16), 77 (17), 51 (12), 51 (12). HRMS (EI): Calculated for C₁₆H₁₀Br₂S [M]⁺ 391.88645 found 391.88593, calculated for C₁₆H₁₀Br⁸¹BrS [M]⁺ 393.88440, calculated for C₁₆H₁₀⁸¹Br₂S₁ [M]⁺ 395.88209 found 395.88209.

3-Bromo-2-(2-bromophenyl)-5-(4-chlorophenyl)thiophene (9b): Yellow oil, 37% yield. ¹H NMR (300 MHz, Chloroform-*d*) $\delta = 7.73 - 7.68$ (m, 1H, CH_{Ar}), 7.52 (m, 2H, CH_{Ar}), 7.46 -7.34 (m, 4H, CH_{Ar}), 7.31 (m, 1H, CH_{Ar}), 7.25 (s, 1H, CH_{thiophene}). ¹³C NMR (75 MHz, CDCl₃) $\delta = 143.3$ (C_{Ar}), 136.7 (C_{Ar}), 134.3 (C_{Ar}), 133.7 (C_{Ar}), 133.2 (CH_{Ar}), 132.9 (CH_{Ar}), 131.7 (C_{Ar}), 130.7 (CH_{Ar}), 129.4 (2CH_{Ar}), 127.4 (CH_{Ar}), 127.0 (2CH_{Ar}), 126.3 (CH_{Ar}), 125.1 (C_{Ar}), 111.8 (C_{Ar}). IR (ATR, cm⁻¹): $\tilde{v} = 3053$ (w), 1502 (w), 1472 (s), 1446 (m), 1402 (w), 1324 (w), 1091

(s), 1054 (m), 1012 (m), 974 (w), 812 (s), 750 (s), 704 (w), 669 (m), 642 (w). MS (EI, 70 eV): m/z (%) = 432 (17), 431 (16), 430 (73), 429 (17), 428 [M⁺] (100), 426 (42), 270 (13), 268 (35), 232 (12), 189 (14). HRMS (EI): Calculated for C₁₆H₉Br₂CIS [M]⁺ 425.84725 found 425.84725, calculated for C₁₆H₉Br⁸¹BrCIS [M]⁺ 427.84543 found 427.84523, calculated for C₁₆H₉Br₂³⁷CIS [M]⁺ 427.84453 found 427.84526, calculated for C₁₆H₉⁸¹Br₂CIS [M]⁺ 429.84338 found 429.84322, calculated for C₁₀H₅⁷⁹Br⁸¹Br³⁷CIS [M]⁺ 429.84248 found 429.84322.

3-Bromo-2-(2-bromophenyl)-5-(4-fluorophenyl)thiophene (9c): White solid, mp. 66 – 67 °C, 33% yield. ¹H NMR (250 MHz, Chloroform-*d*) δ = 7.82 – 7.76 (m, 1H, CH_{Ar}), 7.68 – 7.58 (m, 2H, CH_{Ar}), 7.55 – 7.43 (m, 2H, CH_{Ar}), 7.43 – 7.33 (m, 1H, CH_{Ar}), 7.28 (s, 1H, CH_{thiophene}), 7.24 – 7.13 (m, 2H, CH_{Ar}). ¹⁹F NMR (235 MHz, CDCl₃) δ = -113.03 (CF_{Ar}). ¹³C NMR (63 MHz, CDCl₃) δ = 162.9 (d, ¹*J*_{C-F} = 248.5 Hz, FC_{Ar}), 143.6 (C_{Ar}), 133.8 (C_{Ar}), 133.3 (CH_{Ar}), 133.0 (CH_{Ar}), 130.7 (CH_{Ar}), 129.6 (C_{Ar}), 129.5 (C_{Ar}), 127.6 (d, ³*J*_{C-F} = 8.2 Hz, 2CH_{Ar}), 127.4 (CH_{Ar}), 126.0 (d, ⁴*J*_{C-F} = 1.3 Hz, CH_{Ar}), 125.1 (C_{Ar}), 116.3 (d, ²*J*_{C-F} = 21.9 Hz, 2CH_{Ar}), 111.7 (C_{Ar}). IR (ATR, cm⁻¹): \tilde{v} = 3040 (w), 1539 (w), 1508 (m), 1480 (s), 1423 (m), 1330 (m), 1300 (s), 1162 (s), 1097 (m), 1053 (m), 972 (m), 944 (m), 828 (s), 809 (s), 765 (s), 728 (s), 702 (m), 686 (s), 644 (s), 579 (s). MS (EI, 70 eV): *m/z* (%) = 414 (52), 413 (18), 412 [M⁺] (100), 410 (49), 253 (10), 252 (61), 220 (12), 207 (21), 139 (10). HRMS (EI): Calculated for C₁₆H₉Br₂FS [M]⁺ 409.87703 found 409.87680, calculated for C₁₆H₉Br⁸¹BrFS [M]⁺ 411.87498 found 411.87474, calculated for C₂₀H₁₈⁸¹Br₂FS [M]⁺ 413.87293 found 413.87281.

3-Bromo-2-(2-bromophenyl)-5-(4-(*tert***-butyl)phenyl)thiophene (9d):** White solid, mp. 96 – 97 °C, 26% yield. ¹H NMR (300 MHz, Chloroform-*d*) δ = 7.70 (dd, ³*J* = 7.9 Hz, ⁴*J* = 0.9 Hz, 1H, CH_{Ar}), 7.55 – 7.50 (m, 2H, CH_{Ar}), 7.45 – 7.42 (m, 2H, CH_{Ar}), 7.42 – 7.40 (m, 1H, CH_{Ar}), 7.37 (dd, ³*J* = 7.6, ⁴*J* = 1.3 Hz, 1H, CH_{Ar}), 7.33 – 7.27 (m, 1H, CH_{Ar}), 7.22 (s, 1H, CH_{thiophene}), 1.35 (s, 9H, *t*Bu). ¹³C NMR (63 MHz, CDCl₃) δ = 151.8 (C_{Ar}), 144.8 (C_{Ar}), 135.9 (C_{Ar}), 134.1 (C_{Ar}), 133.3 (CH_{Ar}), 133.1 (CH_A), 130.6 (C_A), 130.5 (CH_{Ar}), 127.4 (CH_{Ar}), 126.2 (2CH_{Ar}), 125.6 (2CH_{Ar}), 125.5 (CH_{Ar}), 125.2 (C_{Ar}), 111.5 (C_{Ar}), 34.9 (C_{16u}), 31.5 (3CH₃). IR (ATR, cm⁻¹): \tilde{v} = 2959 (m), 2864 (w), 1480 (m), 1458 (m), 1362 (w), 1268 (w), 1109 (w), 974 (w), 817 (s), 752 (s), 726(m), 671(m), 578 (w), 545(s). MS (EI, 70 eV): *m/z* (%) = 453 (11), 452 (37), 451 (16), 450 [M⁺] (75), 448 (35), 438 (12), 437 (55), 436 (24), 435 (100), 433 (52), 407 (11), 260 (11), 258 (11), 234 (14), 202 (11), 189 (9), 124 (15), 115 (10), 113 (12), 41 (19). HRMS (EI): Calculated for C₂₀H₁₈Br₂S [M]⁺ 447.94905 found 447.94886, calculated for C₂₀H₁₈Br⁸¹BrS [M]⁺ 449.94700 found 449.94680, calculated for C₂₀H₁₈⁸¹BrS [M]⁺

General procedure for the synthesis of thieno[3,2-b]indoles

3-Bromo-2-(2-bromophenyl)thiophene (0.15 mmol), amine (0.225 mmol), Pd_2dba_3 (0.0075 mmol), dppf or (*S*)-BINAP (0.0075 mmol) and NaO*t*Bu (0.36 mmol) were added to a dried glass pressure tube. The tube was evacuated and backfilled three times with argon. 2 ml of

dried toluene was added. The mixture was heated to 100 °C for 14 hours until completion (monitored by TLC). After cooling to room temperature, the solvent was removed under reduced pressure. The crude oil was subjected to column chromatography (heptane/ethyl acetate) to obtain the pure product.

4-(*p***-Tolyl)-4***H***-thieno[3,2-***b***]indole (3a): Yellow solid, mp. 92 – 93 °C, 97% yield. ¹H NMR (300 MHz, Chloroform-***d***) δ = 7.82 – 7.77 (m, 1H, CH_{Ar}), 7.55 – 7.50 (m, 1H, CH_{Ar}), 7.47 (d, {}^{3}J = 8.3 Hz, 2H, CH_{Ar}), 7.40 – 7.33 (m, 3H, CH_{Ar}), 7.30 – 7.19 (m, 2H, CH_{Ar}), 7.08 (d, {}^{3}J = 5.2 Hz, 1H, CH_{thiophene}), 2.47 (s, 3H, CH₃). ¹³C NMR (75 MHz, CDCl₃) δ = 145.3 (C_{Ar}), 141.6 (C_{Ar}), 136.8 (C_{Ar}), 136.4 (C_{Ar}), 130.5 (2CH_{Ar}), 126.9 (CH_{Ar}), 125.2 (2CH_{Ar}), 123.0 (CH_{Ar}), 122.4 (C_{Ar}), 120.2 (CH_{Ar}), 119.1 (CH_A), 117.8 (C_A), 111.6 (CH_A), 111.2 (CH_A), 21.3 (CH₃). IR (ATR, cm⁻¹): \tilde{v} = 3393 (w), 3109 (w), 3080 (w), 3056 (w), 3030 (w), 2917 (w), 2857 (w), 1600 (m), 1510 (s), 1450 (s), 1392 (m), 1337 (m), 1200 (m), 1085 (m), 1044 (m), 847 (m), 812 (m), 709 (s), 663 (m), 650 (m), 568 (m), 506 (m), 433 (m). MS (EI, 70 eV):** *m/z* **(%) = 264 (20), 263 [M]⁺ (100), 262 (15), 248 (7), 247 (6), 128 (5). HRMS (EI): Calculated for C₁₇H₁₃NS [M]⁺ 263.07632 found 263.07598.**

4-(o-Tolyl)-4*H***-thieno[3,2-***b***]indole (3b):** Yellow oil, 77% yield. ¹H NMR (250 MHz, Chloroform-*d*) δ = 7.74 – 7.68 (m, 1H, CH_{Ar}), 7.34 – 7.29 (m, 2H, CH_{Ar}), 7.28 – 7.24 (m, 2H, CH_{Ar}), 7.23 (d, ³*J* = 5.2 Hz, 1H, CH_{thiophene}), 7.15 – 7.10 (m, 2H, CH_{Ar}), 7.01 – 6.95 (m, 1H, CH_{Ar}), 6.70 (d, ³*J* = 5.2 Hz, 1H, CH_{thiophene}), 1.94 (s, 3H, CH₃). ¹³C NMR (63 MHz, CDCl₃) δ = 145.8 (C_{Ar}), 142.3 (C_{Ar}), 137.2 (C_{Ar}), 136.5 (C_{Ar}), 131.6 (CH_{Ar}), 128.6 (CH_{Ar}), 128.6 (CH_{Ar}), 127.2 (CH_{Ar}), 127.0 (CH_{Ar}), 122.9 (CH_{Ar}), 122.0 (C_{Ar}), 119.9 (CH_{Ar}), 119.0 (CH_{Ar}), 117.1 (C_{Ar}), 111.3 (CH_{Ar}), 111.2 (CH_{Ar}), 17.9 (CH₃). IR (ATR, cm⁻¹): \tilde{v} = 3048 (w), 2917 (w), 1601 (w), 1505 (m), 1486 (m), 1451 (m), 1486 (m), 1450 (s), 1332 (m), 1082 (m), 820 (m), 734 (s), 649 (s), 431 (m). MS (EI, 70 eV): *m/z* (%) = 264 (21), 263 [M]⁺ (100), 262 (47), 230 (16), 218 (11), 217 (13), HRMS (EI): Calculated for C₁₇H₁₃NS [M]⁺ 263.07632 found 263.07591.

4-Phenyl-4*H***-thieno[3,2-***b***]indole (3c):** Yellow oil, 83% yield. ¹H NMR (300 MHz, Chloroform-*d*) δ = 7.86 – 7.79 (m, 1H, CH_{Ar}), 7.66 – 7.54 (m, 5H, CH_{Ar}), 7.45 – 7.39 (m, 1H, CH_{Ar}), 7.38 (d, ³*J* = 5.2 Hz, 1H, CH_{thiophene}), 7.34 – 7.21 (m, 2H, CH_{Ar}), 7.12 (d, ³*J* = 5.2 Hz, 1H, CH_{thiophene}), 7.34 – 7.21 (m, 2H, CH_{Ar}), 7.12 (d, ³*J* = 5.2 Hz, 1H, CH_{thiophene}). ¹³C NMR (75 MHz, CDCl₃) δ = 145.1 (C_{Ar}), 141.4 (C_{Ar}), 139.0 (C_{Ar}), 129.9 (2CH_{Ph}), 127.0 (CH_{Ar}), 126.9 (CH_{Ar}), 125.2 (2CH_{Ph}), 123.2 (CH_{Ar}), 122.5 (C_{Ar}), 120.4 (CH_{Ar}), 119.1 (CH_{Ar}), 118.1 (C_{Ar}), 111.6 (CH_{Ar}), 111.2 (CH_{Ar}). IR (ATR, cm⁻¹): \tilde{v} = 3083 (w), 3050 (w), 1594 (m), 1505 (s), 1449 (s), 1392 (m), 1337 (m), 1201 (m), 1086 (m), 839 (m), 779 (m), 737 (s), 696 (s), 653 (s), 430 (m). MS (EI, 70 eV): *m/z* (%) = 249 [M]⁺ (100), 217 (6), 204 (9), 172 (5), 128 (8), 77 (9), 51 (13). HRMS (EI): Calculated for C₁₆H₁₁NS [M]⁺ 249.06067 found 249.06073.

4-(3,5-Dimethylphenyl)-4*H***-thieno[3,2-***b***]indole (3d): Yellow solid, mp. 112 – 113 °C, 90% yield. ¹H NMR (250 MHz, Chloroform-***d***) \delta = 7.73 – 7.67 (m, 1H, CH_{Ar}), 7.51 – 7.44 (m, 1H, CH_{Ar}), 7.27 (d, ³***J* **= 5.2 Hz, 1H, CH_{thiophene}), 7.22 – 7.09 (m, 4H, CH_{Ar}), 7.01 (d, ³***J* **= 5.2 Hz, 1H, CH_{thiophene}), 6.95 (s, 1H, CH_{Ar}), 2.33 (s, 6H, CH₃). ¹³C NMR (63 MHz, CDCl₃) \delta = 145.2 (C_{Ar}), 141.4 (C_{Ar}), 139.7 (2C_{Ar}), 138.8 (C_{Ar}), 128.6 (CH_{Ar}), 126.8 (CH_{Ar}), 123.0 (CH_{Ar}), 122.9 (2CH_{Ar}), 122.4 (C_{Ar}), 120.2 (CH_{Ar}), 119.1 (CH_{Ar}), 117.8 (C_{Ar}), 111.8 (CH_{Ar}), 111.3 (CH_{Ar}), 21.5 (2CH₃). IR (ATR, cm⁻¹): \tilde{v} = 3051 (w), 3006 (w), 2956 (m), 2915 (m), 2851 (w), 1731 (m), 1594 (m), 1504 (m), 1449 (m), 1343 (m), 1173 (m), 1090 (m), 839 (m), 815 (m), 738 (s), 701 (m), 568 (s). MS (EI, 70 eV):** *m/z* **(%) = 278 (21), 277 (100), 276 (7), 262 (8), 260 (7), 228 (5), 77 (5). HRMS (EI): Calculated for C₁₈H₁₅NS [M]⁺ 277.09197 found 277.09166.**

4-(2,3-Dihydro-1*H***-inden-5-yl)-4***H***-thieno[3,2-***b***]indole (3e): Yellow solid, mp. 81 – 82 °C, 90% yield. ¹H NMR (250 MHz, Chloroform-***d***) \delta = 7.74 – 7.68 (m, 1H, CH_{Ar}), 7.49 – 7.42 (m, 1H, CH_{Ar}), 7.37 – 7.20 (m, 4H, CH_{Ar}), 7.15 (m, 2H, CH_{Ar}), 7.00 (d, ³***J* **= 5.2 Hz, 1H, CH_{thiophene}), 2.92 (t, ³***J* **= 7.4 Hz, 4H, CH₂), 2.10 (p, ³***J* **= 7.5 Hz, 2H, CH₂). ¹³C NMR (63 MHz, CDCl₃) \delta = 146.2 (C_{Ar}), 145.4 (C_{Ar}), 143.1 (C_{Ar}), 141.7 (C_{Ar}), 137.1 (C_{Ar}), 126.8 (CH_{Ar}), 125.4 (CH_{Ar}), 123.3 (CH_{Ar}), 123.0 (CH_{Ar}), 122.3 (C_{Ar}), 121.4 (CH_{Ar}), 120.1 (CH_{Ar}), 119.0 (CH_{Ar}), 117.6 (C_{Ar}), 111.7 (CH_{Ar}), 111.3 (CH_{Ar}), 33.2 (CH₂), 32.7 (CH₂), 25.8 (CH₂). IR (ATR, cm⁻¹): \tilde{v} = 2933 (w), 2837 (w), 1606 (w), 1505 (m), 1486 (m), 1451 (m), 1344 (m), 1099 (m), 820 (m), 736 (s), 648 (s), 426 (m). MS (EI, 70 eV):** *m/z* **(%) = 289 [M]⁺ (100), 255 (5), 172 (12), 115 (10). HRMS (EI): Calculated for C₁₉H₁₅NS [M]⁺ 289.09197 found 289.09201.**

4-(4-(Methylthio)phenyl)-4*H***-thieno[3,2-***b***]indole (3f):** White solid, mp. 91 – 92 °C, ¹H NMR (250 MHz, Chloroform-*d*) δ = 7.69 – 7.63 (m, 1H, CH_{Ar}), 7.41 – 7.27 (m, 5H, CH_{Ar}), 7.21 (d, ³*J* = 5.2 Hz, 1H, CH_{thiophene}), 7.15 – 7.08 (m, 2H, CH_{Ar}), 6.92 (d, ³*J* = 5.2 Hz, 1H, CH_{thiophene}), 2.41 (s, 3H, SCH₃). ¹³C NMR (63 MHz, CDCl₃) δ = 145.0 (C_{Ar}), 141.3 (C_{Ar}), 137.1 (C_{Ar}), 136.1 (C_{Ar}), 127.9 (2CH_{Ar}), 127.1 (CH_{Ar}), 125.6 (2CH_{Ar}), 123.1 (CH_{Ar}), 122.5 (C_{Ar}), 120.4 (CH_{Ar}), 119.1 (CH_{Ar}), 118.0 (C_{Ar}), 111.4 (CH_{Ar}), 111.0 (CH_{Ar}), 16.2 (SCH₃). IR (ATR, cm⁻¹): \tilde{v} = 3381 (w), 3095 (w), 3082 (w), 3046 (w), 2917 (w), 1591 (w), 1505 (s), 1491 (s), 1450 (s), 1393 (m), 1339 (m), 1294 (m), 1094 (m), 1044 (m), 1012 (m), 814 (s), 750 (s), 709 (m), 662 (s), 506 (m). MS (EI, 70 eV): *m/z* (%) = 295 [M]⁺ (100), 280 (68), 247 (22), 148 (10). HRMS (EI): Calculated for C₁₇H₁₃NS₂ 295.04839 found 295.04844.

4-(4-Methoxyphenyl)-4*H***-thieno[3,2-***b***]indole (3g):** White solid, mp. 124 – 125 °C, 91% yield. ¹H NMR (250 MHz, Chloroform-*d*) δ = 7.77 – 7.65 (m, 1H, CH_{Ar}), 7.46 – 7.34 (m, 3H, CH_{Ar}), 7.27 (d, ³*J* = 5.2 Hz, 1H, CH_{thiophene}), 7.22 – 7.08 (m, 2H, CH_{Ar}), 6.99 (m, 2H, CH_{Ar}), 6.95 (d, ³*J* = 5.2 Hz, 1H, CH_{thiophene}), 3.82 (s, 3H, OCH₃). ¹³C NMR (63 MHz, CDCl₃) δ = 158.5 (C_{Ar}), 145.6 (C_{Ar}), 141.9 (C_{Ar}), 131.8 (C_{Ar}), 126.9 (CH_{Ar}), 126.8 (2CH_{Ar}), 123.0 (CH_{Ar}), 122.2

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(C_{Ar}), 120.1 (CH_{Ar}), 119.1 (CH_{Ar}), 117.5 (C_{Ar}), 115.1 (2CH_{Ar}), 111.4 (CH_{Ar}), 111.0 (CH_{Ar}), 55.7 (OCH₃). IR (ATR, cm⁻¹): \tilde{v} = 3140 (w), 3097 (w), 3082 (w), 2838 (w), 1510 (m), 1243 (m), 1024 (m), 824 (m), 754 (s), 713 (m). MS (EI, 70 eV): *m*/*z* (%) = 279 [M]⁺ (100), 264 (45), 236 (15), 191 (9), 140 (8). HRMS (EI): Calculated for C₁₇H₁₃ONS [M]⁺ 279.07124 found 279.07129.

4-(3-Methoxyphenyl)-4*H***-thieno[3,2-***b***]indole (3h): Yellow oil, 92% yield. ¹H NMR (300 MHz, Chloroform-***d***) \delta = 7.73 – 7.67 (m, 1H, CH_{Ar}), 7.54 – 7.48 (m, 1H, CH_{Ar}), 7.36 (t, ³***J* **= 8.1 Hz, 1H, CH_{Ar}), 7.26 (d, ³***J* **= 5.2 Hz, 1H, CH_{thiophene}), 7.22 – 7.12 (m, 2H, CH_{Ar}), 7.12 – 7.06 (m, 1H, CH_{Ar}), 7.06 – 7.00 (m, 2H, CH_{Ar}), 6.84 (ddd, ³***J* **= 8.4 Hz, ⁴***J* **= 2.5 Hz, ⁵***J* **= 0.9 Hz, 1H, CH_{Ar}), 3.76 (s, 3H, OCH₃). ¹³C NMR (75 MHz, CDCl₃) \delta = 160.8 (C_{Ar}), 145.0 (C_{Ar}), 141.3 (C_{Ar}), 140.1 (C_{Ar}), 130.6 (CH_{Ar}), 127.0 (CH_{Ar}), 123.2 (CH_{Ar}), 122.6 (C_{Ar}), 120.4 (CH_{Ar}), 119.1 (CH_{Ar}), 118.2 (C_{Ar}), 117.4 (CH_{Ar}), 112.5 (CH_{Ar}), 111.7 (CH_{Ar}), 111.3 (CH_{Ar}), 111.0 (CH_{Ar}), 55.6 (OCH₃). IR (ATR, cm⁻¹): \tilde{v} = 3392 (w), 3084 (w), 3051 (w), 3000 (w), 2956 (w), 2833 (w), 1589 (s), 1505 (s), 1489 (s), 1450 (s), 1391 (m), 1340 (m), 1313 (m), 1278 (m), 1252 (m), 1233 (m), 1193 (m), 1160 (m), 1086 (m), 1036 (m), 821 (m), 777 (m), 738 (s), 695 (s), 656 (s), 431 (m). MS (EI, 70 eV):** *m/z* **(%) = 279 (100), 236 (23), 204 (5), 191 (8), 139 (9). HRMS (EI): Calculated for C₁₇H₁₃ONS [M]⁺ 279.07124 found 279.07131.**

4-(2-Methoxyphenyl)-4*H***-thieno[3,2-***b***]indole (3i):** Yellow oil, 87% yield. ¹H NMR (300 MHz, Chloroform-*d*) δ = 7.81 – 7.76 (m, 1H, CH_{Ar}), 7.50 – 7.41 (m, 2H, CH_{Ar}), 7.32 (d, ³*J* = 5.2 Hz, 1H, CH_{thiophene}), 7.25 – 7.18 (m, 3H, CH_{Ar}), 7.18 – 7.08 (m, 2H, CH_{Ar}), 6.88 (d, ³*J* = 5.2 Hz, 1H, CH_{thiophene}), 3.77 (s, 3H, OCH₃). ¹³C NMR (75 MHz, CDCl₃) δ = 155.1 (C_{Ar}), 145.8 (C_{Ar}), 142.2 (C_{Ar}), 129.1 (CH_{Ar}), 128.7 (CH_{Ar}), 127.2 (C_{Ar}), 126.5 (CH_{Ar}), 122.8 (CH_{Ar}), 122.3 (C_{Ar}), 121.2 (CH_{Ar}), 119.9 (CH_{Ar}), 118.9 (CH_{Ar}), 117.4 (C_{Ar}), 112.8 (CH_{Ar}), 112.1 (CH_{Ar}), 111.7 (CH_{Ar}), 55.8 (OCH₃). IR (ATR, cm⁻¹): \tilde{v} = 3396 (w), 3048 (w), 3006 (w), 2958 (w), 2930 (w), 2835 (w), 1594 (m), 1509 (s), 1449 (s), 1393 (m), 1337 (m), 1273 (m), 1243 (m), 1118 (m), 1083 (m), 1021 (m), 702 (m), 654 (m), 430 (m). MS (EI, 70 eV): *m/z* (%) = 279 (100), 263 (20), 236 (11), 204 (5), 191 (7), 139 (8). HRMS (EI): Calculated for C₁₇H₁₃ONS [M]⁺ 279.07124 found 279.07092.

4-(3,5-Dimethoxyphenyl)-4*H***-thieno[3,2-***b***]indole (3j): Yellow oil, 92% yield. ¹H NMR (300 MHz, Chloroform-***d***) \delta = 7.74 - 7.66 (m, 1H, CH_{Ar}), 7.59 - 7.52 (m, 1H, CH_{Ar}), 7.28 (d, ³***J* **= 5.2 Hz, 1H, CH_{thiophene}), 7.24 - 7.11 (m, 2H, CH_{Ar}), 7.07 (d, ³***J* **= 5.2 Hz, 1H, CH_{thiophene}), 6.67 (d, ⁴***J* **= 2.3 Hz, 2H, CH_{Ar}), 6.42 (t, ⁴***J* **= 2.3 Hz, 1H, CH_{Ar}), 3.76 (s, 6H, OCH₃). ¹³C NMR (75 MHz, CDCl₃) \delta = 160.8 (2C_{Ar}OCH₃), 143.9 (C_{Ar}), 140.3 (C_{Ar}), 139.6 (C_{Ar}), 126.0 (CH_{Ar}), 122.2 (CH_{Ar}), 121.6 (C_{Ar}), 119.5 (CH_{Ar}), 118.1 (CH_{Ar}), 117.2 (C_{Ar}), 110.9 (CH_{Ar}), 110.5 (CH_{Ar}), 102.5 (2CH_{Ar}), 98.0 (CH_{Ar}), 54.7 (2OCH₃). IR (ATR, cm⁻¹): \tilde{v} = 3084 (w), 3050 (w), 2959 (w), 2930 (w), 2837 (w), 1590 (s), 1505 (m), 1477 (m), 1449 (s), 1362 (m), 1285 (m), 1267 (m),**

1202 (m), 1150 (s), 1062 (m), 1037 (m), 813 (m), 737 (s). MS (EI, 70 eV): m/z (%) = 310 (20), 309 [M]⁺ (100), 266 (12), 251 (13), 234 (5). HRMS (EI): Calculated for C₁₈H₁₅O₂NS [M]⁺ 309.08180 found 309.08198.

4-(2,4-Dimethoxyphenyl)-4*H***-thieno[3,2-***b***]indole (3k): Colorless solid, mp. 165 – 166 °C, 89% yield. ¹H NMR (250 MHz, Chloroform-***d***) δ = 7.83 – 7.76 (m, 1H, CH_{Ar}), 7.36 (d, ³***J* **= 8.6 Hz, 1H, CH_{Ar}), 7.32 (d, ³***J* **= 5.2 Hz, 1H, CH_{thiophene}), 7.25 – 7.16 (m, 3H, CH_{Ar}), 6.87 (d, ³***J* **= 5.2 Hz, 1H, CH_{thiophene}), 6.71 (d, ⁴***J* **= 2.6 Hz, 1H, CH_{Ar}), 6.63 (dd, ³***J* **= 8.6 Hz, ⁴***J* **= 2.6 Hz, 1H, CH_{Ar}), 3.91 (s, 3H, OCH₃), 3.73 (s, 3H, OCH₃). ¹³C NMR (63 MHz, CDCl₃) δ = 160.5 (C_{Ar}), 156.3 (C_{Ar}), 146.2 (C_{Ar}), 142.5 (C_{Ar}), 129.4 (CH_{Ar}), 126.4 (CH_{Ar}), 122.7 (CH_{Ar}), 122.1 (C_{Ar}), 120.2 (C_{Ar}), 119.7 (CH_{Ar}), 118.9 (CH_{Ar}), 116.9 (C_{Ar}), 111.9 (CH_{Ar}), 111.5 (CH_{Ar}), 104.8 (CH_{Ar}), 100.2 (CH_{Ar}), 55.8 (OCH₃), 55.8 (OCH₃). IR (ATR, cm⁻¹): \tilde{v} = 3087 (w), 3045 (w), 3005 (w), 2965 (w), 2931 (w), 2835 (w), 1611 (m), 1584 (m), 1518 (s), 1451 (s), 1305 (m), 1204 (s), 1158 (s), 1050 (m), 1022 (m), 928 (w), 827 (m), 740 (s), 651 (m), 581 (m). MS (EI, 70 eV):** *m/z* **(%) = 309 (100), 294 (19), 251 (12), 223 (8). HRMS (EI): Calculated for C₁₈H₁₅O₂NS [M]⁺ 309.08180 found 309.08151.**

4-(3,4,5-Trimethoxyphenyl)-4*H***-thieno[3,2-***b***]indole (3I):** White solid, mp. 94 – 95 °C, 92% yield. ¹H NMR (250 MHz, Chloroform-*d*) δ = 7.75 – 7.67 (m, 1H, CH_{Ar}), 7.52 – 7.46 (m, 1H, CH_{Ar}), 7.30 (d, ³*J* = 5.2 Hz, 1H, CH_{thiophene}), 7.26 – 7.10 (m, 2H, CH_{Ar}), 7.02 (d, ³*J* = 5.2 Hz, 1H, CH_{thiophene}), 6.72 (s, 2H, CH_{Ar}), 3.87 (s, 3H, OCH₃), 3.80 (s, 6H, OCH₃). ¹³C NMR (63 MHz, CDCl₃) δ = 154.1 (2C_{Ar}OCH₃), 145.2 (C_{Ar}), 141.6 (C_{Ar}), 137.0 (C_{Ar}), 134.7 (C_{Ar}), 127.1 (CH_{Ar}), 123.2 (CH_{Ar}), 122.4 (C_{Ar}), 120.4 (CH_{Ar}), 119.2 (CH_{Ar}), 117.9 (C_{Ar}), 111.6 (CH_{Ar}), 111.2 (CH_{Ar}), 103.0 (2CH_{Ar}), 61.2 (OCH₃), 56.5 (2OCH₃). IR (ATR, cm⁻¹): \tilde{v} = 3082 (w), 3051 (w), 2926 (m), 2824 (w), 1593 (m), 1505 (m). MS (EI, 70 eV): *m/z* (%) = 339 (100), 324 (75), 296 (10), 266 (9), 210 (9), 172 (13), 154 (8). HRMS (EI): Calculated for C₁₉H₁₇O₃NS [M]⁺ 339.09237 found 339.09217.

4-(4-(*tert***-Butyl)phenyl)-4***H***-thieno[3,2-***b***]indole (3m): Yellow oil, 92% yield. ¹H NMR (250 MHz, Chloroform-***d***) δ = 7.75 – 7.67 (m, 1H, CH_{Ar}), 7.52 – 7.39 (m, 5H, CH_{Ar}), 7.26 (d, {}^{3}J = 5.2 Hz, 1H, CH_{thiophene}), 7.20 – 7.12 (m, 2H, CH_{Ar}), 7.02 (d, {}^{3}J = 5.2 Hz, 1H, CH_{thiophene}), 7.20 – 7.12 (m, 2H, CH_{Ar}), 7.02 (d, {}^{3}J = 5.2 Hz, 1H, CH_{thiophene}), 1.32 (s, 9H,** *t***Bu). ¹³C NMR (63 MHz, CDCl₃) δ = 149.9 (C_{Ar}), 145.2 (C_{Ar}), 141.5 (C_{Ar}), 136.3 (C_{Ar}), 126.9 (CH_{Ar}), 126.7 (2CH_{Ar}), 124.7 (2CH_{Ar}), 123.0 (CH_{Ar}), 122.4 (C_{Ar}), 120.2 (CH_{Ar}), 119.1 (CH_{Ar}), 117.8 (C_{Ar}), 111.7 (CH_{Ar}), 111.3 (CH_{Ar}), 34.9 (C_{***t***Bu}), 31.6 (3CH₃). IR (ATR, cm⁻¹): \tilde{v} = 3049 (w), 2959 (m), 2901 (w), 2865 (w), 1602 (w), 1519 (s), 1451 (s), 1394 (m), 1337 (m), 1267 (m), 1205 (m), 1112 (m), 1086 (m), 1046 (m), 1016 (m), 922 (w), 825 (m), 705 (m), 648 (m), 552 (m). MS (EI, 70 eV):** *m/z* **(%) = 305 (100), 290 (95), 275 (16), 262 (11), 172 (17), 131 (11). HRMS (EI): Calculated for C₂₀H₁₉NS [M]⁺ 305.12327 found 305.12374.**

4-(Naphthalen-1-yl)-4*H***-thieno[3,2-***b***]indole (3n): Colorless solid, mp. 141 – 142 °C, 78% yield. ¹H NMR (300 MHz, Acetone-d_6) \delta = 8.19 - 8.09 (m, 2H, CH_{Ar}), 7.92 – 7.87 (m, 1H, CH_{Ar}), 7.79 – 7.70 (m, 2H, CH_{Ar}), 7.61 (ddd, ³***J* **= 8.2 Hz, ³***J* **= 6.8 Hz, ⁴***J* **= 1.3 Hz, 1H, CH_{Ar}), 7.54 (d, ³***J* **= 5.2 Hz, 1H, CH_{thiophene}), 7.45 (ddd, ³***J* **= 8.2 Hz, ³***J* **= 6.8 Hz, ⁴***J* **= 1.3 Hz, 1H, CH_{Ar}), 7.32 – 7.27 (m, 1H, CH_{Ar}), 7.27 – 7.16 (m, 2H, CH_{Ar}), 7.06 – 6.99 (m, 1H, CH_{Ar}), 6.79 (d, ³***J* **= 5.2 Hz, 1H, CH_{thiophene}). ¹³C NMR (75 MHz, Acetone-d_6) \delta = 147.6 (C_{Ar}), 144.0 (C_{Ar}), 135.8 (C_{Ar}), 135.6 (C_{Ar}), 131.2 (C_{Ar}), 129.8 (CH_{Ar}), 129.5 (CH_{Ar}), 128.4 (CH_{Ar}), 128.0 (CH_{Ar}), 127.7 (CH_{Ar}), 126.9 (CH_{Ar}), 126.7 (CH_{Ar}), 123.9 (CH_{Ar}), 123.8 (CH_{Ar}), 123.0 (C_{Ar}), 121.1 (CH_{Ar}), 119.7 (CH_{Ar}), 117.9 (C_{Ar}), 112.3 (CH_{Ar}), 112.1 (CH_{Ar}). IR (ATR, cm⁻¹): \tilde{v} = 3047 (m), 1592 (w), 1575 (w), 1504 (m), 1448 (m), 1401 (m), 1327 (m), 1211 (m), 1110 (m), 1076 (m), 1914 (m), 800 (m), 773 (m), 735 (s), 657 (m). MS (EI, 70 eV):** *m/z* **(%) = 299 (100), 265 (18), 149 (8), 127 (7). HRMS (EI): Calculated for C₂₀H₁₃NS [M]⁺ 299.07632 found 299.07610.**

4-(Anthracen-2-yl)-4*H***-thieno[3,2-***b***]indole (3o):** Yellow solid, mp. 176 – 177 °C, 72% yield. ¹H NMR (250 MHz, Chloroform-*d*) δ = 8.53 (s, 1H, CH_{Ar}), 8.47 (s, 1H, CH_{Ar}), 8.25 – 8.14 (m, 2H, CH_{Ar}), 8.05 (m, 2H, CH_{Ar}), 7.90 – 7.78 (m, 1H, CH_{Ar}), 7.78 – 7.65 (m, 2H, CH_{Ar}), 7.59 – 7.47 (m, 2H, CH_{Ar}), 7.42 (d, ³*J* = 5.2 Hz, 1H, CH_{thiophene}), 7.37 – 7.18 (m, 3H, CH_{Ar}). ¹³C NMR (63 MHz, CDCl₃) δ = 145.2 (C_{Ar}), 141.5 (C_{Ar}), 135.7 (C_{Ar}), 132.3 (C_{Ar}), 131.9 (C_{Ar}), 131.7 (C_{Ar}), 130.2 (CH_{Ar}), 120.1 (C_{Ar}), 128.3 (CH_{Ar}), 128.0 (CH_{Ar}), 127.0 (CH_{Ar}), 126.5 (CH_{Ar}), 126.1 (CH_{Ar}), 126.0 (CH_{Ar}), 125.7 (CH_{Ar}), 123.7 (CH_{Ar}), 123.1 (CH_{Ar}), 122.6 (C_{Ar}), 122.3 (CH_{Ar}), 120.5 (CH_{Ar}), 119.1 (CH_{Ar}), 111.8 (C_{Ar}), 111.4 (CH_{Ar}). IR (ATR, cm⁻¹): \tilde{v} = 3049 (w), 2954 (w), 1670 (w), 1592 (w), 1504 (m), 1450 (m), 1321 (m), 887 (m), 738 (s), 652 (m), 603 (m), 469 (m), 429 (m). MS (EI, 70 eV): *m/z* (%) = 349 (100), 315 (4), 176 (7). HRMS (EI): Calculated for C₂₄H₁₅NS [M]⁺ 349.09197 found 349.09165.

4-(4-Fluorophenyl)-4*H***-thieno[3,2-***b***]indole (3p):** White solid, mp. 117 – 118 °C, 91% yield. ¹H NMR (300 MHz, Chloroform-*d*) δ = 7.75 – 7.68 (m, 1H, CH_{Ar}), 7.50 – 7.41 (m, 2H, CH_{Ar}), 7.40 – 7.36 (m, 1H, CH_{Ar}), 7.28 (d, ³*J* = 5.2 Hz, 1H, CH_{thiophene}), 7.23 – 7.11 (m, 4H, CH_{Ar}), 6.95 (d, ³*J* = 5.2 Hz, 1H, CH_{thiophene}). ¹⁹F NMR (282 MHz, CDCl₃) δ = -114.59 (FC_{Ar}). ¹³C NMR (75 MHz, CDCl₃) δ = 161.2 (d, ¹*J*_{C-F} = 246.7 Hz, CF_{Ar}), 145.2 (C_{Ar}), 141.6 (C_{Ar}), 134.6 (d, ⁴*J*_{C-F} = 3.1 Hz, C_{Ar}), 127.1 (CH_{Ar}), 127.0 (d, ³*J*_{C-F} = 8.5 Hz, 2CH_{Ar}), 123.2 (CH_{Ar}), 122.3 (C_{Ar}), 120.4 (CH_{Ar}), 119.1 (CH_{Ar}), 118.0 (C_{Ar}), 116.7 (d, ²*J*_{C-F} = 22.8 Hz, 2CH_{Ar}), 111.2 (CH_{Ar}), 110.9 (CH_{Ar}). IR (ATR, cm⁻¹): \tilde{v} = 3106 (w), 3093 (w), 3050 (w), 1600 (w), 1510 (s), 1451 (m), 1340 (m), 1218 (m), 1090 (m), 826 (m), 740 (s), 708 (m), 571 (m), 515 (m). MS (EI, 70 eV): *m/z* (%) = 267 (100), 235 (9), 222 (9), 128 (5), 75 (10). HRMS (EI): Calculated for C₁₆H₁₀NFS [M]⁺ 267.05125 found 267.05098.

4-(4-Chlorophenyl)-4*H***-thieno[3,2-***b***]indole** (3q): Colorless solid, mp. 114 – 115 °C, 86% yield. ¹H NMR (250 MHz, Chloroform-*d*) δ = 7.76 – 7.69 (m, 1H, CH_{Ar}), 7.46 (m, 5H,

CH_{Ar}), 7.31 (d, ${}^{3}J$ = 5.2 Hz, 1H, CH_{thiophene}), 7.25 – 7.13 (m, 2H, CH_{Ar}), 6.99 (d, ${}^{3}J$ = 5.2 Hz, 1H, CH_{thiophene}). 13 C NMR (63 MHz, CDCl₃) δ = 144.8 (C_{Ar}), 141.2 (C_{Ar}), 137.6 (C_{Ar}), 132.4 (C_{Ar}), 130.1 (2CH_{Ar}), 127.3 (CH_{Ar}), 126.4 (2CH_{Ar}), 123.4 (CH_{Ar}), 122.6 (C_{Ar}), 120.7 (CH_{Ar}), 119.3 (CH_{Ar}), 118.5 (C_{Ar}), 111.3 (CH_{Ar}), 110.9 (CH_{Ar}). IR (ATR, cm⁻¹): \tilde{v} = 3099 (w), 3084 (w), 3050 (w), 2959 (w), 2920 (w), 2848 (w), 1592 (w), 1505 (s), 1488 (m), 1452 (m), 1390 (m), 1356 (w), 1338 (m), 1204 (m), 1088 (s), 1012 (m), 823 (s), 748 (s), 708 (s), 661 (m), 646 (m), 509 (m), 479 (m), 431 (w). MS (EI, 70 eV): *m/z* (%) = 285 (32), 283 (100), 247 (12), 128 (10), 75 (18). HRMS (EI): Calculated for C₁₆H₁₀NCIS 283.02170 found 283.02225, calculated for C₁₆H₁₀N³⁷CIS [M]⁺ 285.01875 found 285.01936.

4-Benzyl-4*H***-thieno[3,2-***b***]indole (3***r***): Yellow oil, 81% yield. ¹H NMR (250 MHz, Chloroform-***d***) δ = 7.69 (ddd, ³***J* **= 7.6 Hz, ⁴***J* **= 1.5 Hz, ⁵***J* **= 0.7 Hz, 1H, CH_{Ar}), 7.25 (dd, ⁴***J* **= 1.4 Hz, ⁵***J* **= 0.8 Hz, 1H, CH_{Ar}), 7.23 (d, ³***J* **= 5.2 Hz, 1H, CH_{thiophene}), 7.21 – 7.11 (m, 5H, CH_{Ar}), 7.11 – 7.03 (m, 2H, CH_{Ar}), 6.84 (d, ³***J* **= 5.2 Hz, 1H, CH_{thiophene}), 5.36 (s, 2H_{aliphatic}, CH₂). ¹³C NMR (63 MHz, CDCl₃) δ = 145.6 (C_{Ar}), 141.7 (C_{Ar}), 137.3 (C_{Ar}), 128.9 (2CH_{Ar}), 127.7 (CH_{Ar}), 127.0 (CH_{Ar}), 126.8 (2CH_{Ar}), 122.7 (CH_{Ar}), 122.1 (C_{Ar}), 119.5 (CH_{Ar}), 119.1 (CH_{Ar}), 116.7 (C_{Ar}), 110.7 (CH_{Ar}), 110.3 (CH_{Ar}), 48.9 (CH₂). IR (ATR, cm⁻¹): \tilde{v} = 3422 (w), 3081 (w), 3054 (w), 3025 (w), 2921 (w), 2852 (w), 1733 (w), 1583 (w), 1507 (m), 1463 (m), 1349 (m), 1161 (m), 736 (s), 695 (m), 654 (s), 430 (m). MS (EI, 70 eV):** *m/z* **(%) = 264 (15), 263 [M]⁺ (71), 172 (27), 128 (13), 91 (100), 65 (17). HRMS (EI): Calculated for C₁₇H₁₃NS [M]⁺ 263.07632 found 263.07642.**

4-(4-methoxybenzyl)-4*H***-thieno[3,2-***b***]indole (3s):** Colorless oil, 95% yield. ¹H NMR (250 MHz, Chloroform-*d*) δ = 7.68 (m, 1H, CH_{Ar}), 7.28 (d, ³*J* = 8.3, 1H, CH_{Ar}), 7.22 (d, ³*J* = 5.2 Hz, 1H, CH_{thiophene}), 7.20 – 7.12 (m, 1H, CH_{Ar}), 7.12 – 7.04 (m, 1H, CH_{Ar}), 7.00 (d, ³*J* = 8.6 Hz, 2H, CH_{Ar}), 6.82 (d, ³*J* = 5.2 Hz, 1H, CH_{thiophene}), 6.70 (d, ³*J* = 8.6 Hz, 2H, CH_{Ar}), 5.28 (s, 2H_{aliphatic}, CH₂), 3.65 (s, 3H, OCH₃). ¹³C NMR (63 MHz, CDCl₃) δ = 159.2 (C_{Ar}), 145.5 (C_{Ar}), 141.7 (C_{Ar}), 129.4 (C_{Ar}), 128.2 (2CH_{Ar}), 126.9 (CH_{Ar}), 122.7 (CH_{Ar}), 122.1 (C_{Ar}), 119.4 (CH_{Ar}), 119.1 (CH_{Ar}), 116.6 (C_{Ar}), 114.3 (2CH_{Ar}), 110.7 (CH_{Ar}), 110.3 (CH_{Ar}), 55.4 (OCH₃), 48.4 (CH₂). IR (ATR, cm⁻¹): \tilde{v} = 3105 (w), 3051 (w), 3024 (w), 2997 (m), 2955 (m), 2915 (w), 2832 (m), 1613 (m), 1584 (m), 1508 (s), 1457 (s), 1439 (m), 1348 (m), 1245 (s), 1161 (s), 1025 (m), 807 (s), 735 (s), 653 (s), 430 (m). MS (EI, 70 eV): *m/z* (%) = 294 (6), 293 [M]⁺ (28), 121 (100), 78 (10). HRMS (EI): Calculated for C₁₈H₁₅ONS [M]⁺ 293.08689 found 293.08643.

4-Pentyl-4*H***-thieno[3,2-***b***]indole (3t):** Yellow oil, 75% yield. ¹H NMR (250 MHz, Chloroform-*d*) $\delta = 7.76$ (ddd, ³*J* = 7.8 Hz, ⁴*J* = 1.3 Hz, ⁵*J* = 0.7 Hz, 1H, CH_{Ar}), 7.43 – 7.35 (m, 2H, CH_{Ar}), 7.34 – 7.26 (m, 1H, CH_{Ar}), 7.17 (ddd, ³*J* = 8.1 Hz, ³*J* = 7.0 Hz, ⁴*J* = 1.2 Hz, 1H, CH_{Ar}), 7.08 (d, ³*J* = 5.2 Hz, 1H, CH_{thiophene}), 4.27 (t, ³*J* = 7.1 Hz, 2H_{aliphatic}, CH₂), 2.00 – 1.74 (m, 2H_{aliphatic}, CH₂), 1.34 (m, 4H_{aliphatic}, 2CH₂), 0.98 – 0.80 (m, 3H_{aliphatic}, CH₃). ¹³C NMR (63

MHz, CDCl₃) $\delta = 145.5$ (C_{Ar}), 141.4 (C_{Ar}), 126.8 (CH_{Ar}), 122.4 (CH_{Ar}), 121.9 (C_{Ar}), 119.1 (CH_{Ar}), 119.0 (CH_{Ar}), 116.0 (C_{Ar}), 110.5 (CH_{Ar}), 110.0 (CH_{Ar}), 45.4 (CH₂, pentyl), 29.6 (CH₂, pentyl), 29.4 (CH₂, pentyl), 22.5 (CH₂, pentyl), 14.1 (CH₃, pentyl). IR (ATR, cm⁻¹): $\tilde{v} = 3081$ (w), 3052 (w), 2954 (m), 2927 (m), 2856 (m), 1610 (w), 1509 (m), 1123 (m), 1348 (m), 1317 (m), 1162 (m), 1079 (m), 1017 (w), 815 (w), 735 (s), 653 (m), 431 (m). MS (EI, 70 eV): m/z (%) = 243 [M]⁺ (30), 186 (100), 115 (12). HRMS (EI): Calculated for C₁₅H₁₇NS [M]⁺ 243.10762 found 243.10811.

General procedure for the synthesis of thieno[3,4-b]indoles

3-Bromo-2-(2-bromophenyl)thiophene (0.15 mmol), amine (0.225 mmol), Pd_2dba_3 (0.0075 mmol), $PtBu_3 \cdot HBF_4$ (0.015 mmol) and NaO*t*Bu (0.36 mmol) were added to a dried glass pressure tube. The tube was evacuated and backfilled three times with argon. 2 ml of dried toluene was added. The mixture was heated to 100 °C for 14h until the reaction completed (monitored by TLC). After cooling to room temperature, the solvent was removed under reduced pressure. The crude oil was subjected to column chromatography (heptane/ethyl acetate) to obtain the pure product.

4-(*p***-Tolyl)-4***H***-thieno[3,4-***b***]indole (6a): Yellow oil, 95% yield. ¹H NMR (250 MHz, Chloroform-***d***) \delta = 7.86 (dt, ³***J* **= 7.6 Hz, ⁴***J* **= 1.0 Hz, 1H, CH_{Ar}), 7.54 (m, 1H, CH_{Ar}), 7.50 (s, 1H, CH_{Ar}), 7.49 (s, 1H, CH_{Ar}), 7.31 – 7.21 (m, 4H, CH_{Ar}), 7.14 (ddd, ³***J* **= 7.6 Hz, ³***J* **= 6.6 Hz, ⁴***J* **= 1.7 Hz, 1H, CH_{Ar}), 6.59 (m, 1H, CH_{Ar}), 2.36 (s, 3H, CH₃). ¹³C NMR (63 MHz, CDCl₃) \delta = 148.1 (C_{Ar}), 146.3 (C_{Ar}), 136.8 (C_{Ar}), 136.1 (C_{Ar}), 133.5 (C_{Ar}), 130.5 (2CH_{Ar}), 126.5 (CH_{Ar}), 124.4 (2CH_{Ar}), 121.5 (CH_{Ar}), 120.3 (C_{Ar}), 119.8 (CH_{Ar}), 110.6 (CH_{Ar}), 109.9 (CH_{Ar}), 92.6 (CH_{Ar}), 21.3 (CH₃). IR (ATR, cm⁻¹): \tilde{v} = 3399 (w), 3101 (w), 3030 (w), 2917 (w), 2859 (w), 1608 (w), 1576 (m), 1512 (s), 1449 (m), 1397 (m), 1321 (m), 1223 (m), 1152 (m), 1108 (w), 1020 (w), 928 (w), 816 (m), 740 (s), 619 (m), 499 (m). MS (EI, 70 eV):** *m/z* **(%) = 263 (100), 247 (8), 218 (12), 128 (7). HRMS (EI): Calculated for C₁₇H₁₃NS [M]⁺ 263.07632 found 263.07634.**

4-(o-Tolyl)-4*H***-thieno[3,4-***b***]indole (6b): Yellow oil, 65% yield. ¹H NMR (300 MHz, Acetone-***d***₆) δ = 8.02 – 7.92 (m, 2H, CH_{Ar}), 7.89 – 7.79 (m, 1H, CH_{Ar}), 7.79 (d, ⁴***J* **= 2.5 Hz, 1H, CH_{thiophene}), 7.58 (d, ³***J* **= 8.2 Hz, 1H, CH_{Ar}), 7.48 – 7.32 (m, 2H, CH_{Ar}), 7.16 (m, 1H, CH_{Ar}), 6.93 (d, ³***J* **= 8.2 Hz, 1H, CH_{Ar}), 6.51 (d, ⁴***J* **= 2.5 Hz, 1H, CH_{thiophene}), 2.22 (s, 3H, CH₃). ¹³C NMR (75 MHz, Acetone-***d***₆) δ = 149.9 (C_{Ar}), 147.5 (C_{Ar}), 141.0 (C_{Ar}), 137.8 (C_{Ar}), 134.1 (C_{Ar}), 131.2 (CH_{Ar}), 129.5 (CH_{Ar}), 127.5 (CH_{Ar}), 126.9 (CH_{Ar}), 122.3 (CH_{Ar}), 121.3 (CH_{Ar}), 120.8 (C_{Ar}), 120.4 (CH_{Ar}), 112.0 (CH_{Ar}), 110.5 (CH_{Ar}), 93.2 (CH_{Ar}), 18.2 (CH₃). IR (ATR, cm⁻¹): \tilde{v} = 3412 (w), 3103 (w), 3052 (w), 2919 (w), 2853 (w), 1577 (m), 1499 (m), 1450 (m), 1395**

(m), 1316 (m), 1227 (m), 1151 (m), 824 (m), 741 (s), 622 (m), 445 (m). MS (EI, 70 eV): m/z (%) = 264 (21), 263 [M]⁺ (100), 262 (41), 260 (11), 231 (16), 228 (11), 218 (20), 217 (32), 216 (11), 204 (15), 128 (17). HRMS (EI): Calculated for C₁₇H₁₃NS [M]⁺ 263.07632 found 263.07567.

4-(4-(*tert***-Butyl)phenyl)-4***H***-thieno[3,4-***b***]indole (6c): Yellow oil, 83% yield. ¹H NMR (250 MHz, Chloroform-***d***) δ = 7.78 (m, 1H, CH_{Ar}), 7.48 (m, 4H, CH_{Ar}), 7.41 (s, 1H_{Ar}), 7.33 (ddd, {}^{3}J = 8.3 Hz, {}^{4}J = 1.2 Hz, {}^{5}J = 0.7 Hz, 1H, CH_{Ar}), 7.25 (dd, {}^{3}J = 7.1 Hz, {}^{4}J = 1.3 Hz, 1H, CH_{Ar}), 7.18 (s, 1H, CH_{Ar}), 7.09 – 7.02 (m, 1H, CH_{Ar}), 1.33 (s, 9H,** *t***Bu). ¹³C NMR (63 MHz, CDCl₃) δ = 149.2 (C_{Ar}), 148.1 (C_{Ar}), 146.2 (C_{Ar}), 136.8 (C_{Ar}), 133.5 (C_{Ar}), 126.8 (2CH_{Ar}), 126.5 (CH_{Ar}), 123.9 (2CH_{Ar}), 121.5 (CH_{Ar}), 120.4 (C_{Ar}), 119.8 (CH_{Ar}), 110.5 (CH_{Ar}), 110.0 (CH_{Ar}), 92.7 (CH_{Ar}), 34.8 (C_{Bu}), 31.6 (3CH₃). IR (ATR, cm⁻¹): \tilde{v} = 3401 (w), 3053 (w), 2958 (m), 2865 (w), 1605 (w), 1578 (m), 1517 (s), 1451 (m), 1399 (m), 1323 (m), 1224 (m), 1190 (m), 1152 (m), 1017 (w), 827 (m), 742 (s), 622 (m), 552 (m). MS (EI, 70 eV):** *m/z* **(%) = 305 [M]⁺ (97), 290 (100), 275 (18), 262 (8), 172 (20), 131 (40), 109 (9). HRMS (EI): Calculated for C₂₀H₁₉NS [M]⁺ 305.12327 found 305.12400.**

4-(3,5-Dimethoxyphenyl)-4*H***-thieno[3,4-***b***]indole (6d): Yellow oil, 85% yield. ¹H NMR (300 MHz, Chloroform-***d***) δ = 7.85 (m, 1H, CH_{Ar}), 7.52 – 7.45 (m, 2H, CH_{Ar}), 7.33 (ddd, ³***J* **= 8.4 Hz, ³***J* **= 7.3 Hz, ⁴***J* **= 1.3 Hz, 1H, CH_{Ar}), 7.15 (td, ³***J* **= 7.3 Hz, ⁴***J* **= 1.3 Hz, 1H, CH_{Ar}), 6.81 (d, ⁴***J* **= 2.3 Hz, 2H, CH_{Ar}), 6.68 (d, ⁴***J* **= 2.5 Hz, 1H, CH_{thiophene}), 6.45 (t, ⁴***J* **= 2.3 Hz, 1H, CH_{Ar}), 3.85 (s, 6H, OCH₃). ¹³C NMR (75 MHz, CDCl₃) δ = 161.9 (2C_{Ar}), 147.7 (C_{Ar}), 145.8 (C_{Ar}), 141.2 (C_{Ar}), 133.5 (C_{Ar}), 126.6 (CH_{Ar}), 121.5 (CH_{Ar}), 120.6 (C_{Ar}), 120.1 (CH_{Ar}), 110.8 (CH_{Ar}), 110.4 (CH_{Ar}), 102.6 (2CH_{Ar}), 98.4 (CH_{Ar}), 93.3 (CH_{Ar}), 55.7 (2OCH₃). IR (ATR, cm⁻¹): \tilde{v} = 3388 (w), 3102 (w), 3056 (w), 2998 (w), 2929 (w), 2837 (w), 1591 (s), 1498 (m), 1451 (s), 1293 (m), 1258 (s), 1202 (s), 1149 (s), 1056 (m), 929 (m), 823 (m), 742 (s), 689 (m), 627 (m). MS (EI, 70 eV):** *m/z* **(%) = 310 (21), 309 [M]⁺ (100), 294 (22), 264 (8), 251 (19), 250 (18), 234 (10), 191 (6), 178 (11), 128 (9). HRMS (EI): Calculated for C₁₈H₁₅O₂NS [M]⁺ 309.08180 found 309.08182.**

4-(3,4,5-Trimethoxyphenyl)-4*H***-thieno[3,4-***b***]indole (6e):** Colorless solid, mp. 96 – 97 °C, 81% yield. ¹H NMR (300 MHz, Chloroform-*d*) δ = 7.87 (ddd, ³*J* = 7.7 Hz, ⁴*J* = 1.3 Hz, ⁵*J* = 0.7 Hz, 1H, CH_{Ar}), 7.50 (d, ⁴*J* = 1.8 Hz, 1H, CH_{thiophene}), 7.40 (ddd, ³*J* = 8.2 Hz, ⁴*J* = 1.3 Hz, ⁵*J* = 0.7 Hz, 1H, CH_{Ar}), 7.33 (ddd, ³*J* = 8.2 Hz, ³*J* = 7.0 Hz, ⁴*J* = 1.3 Hz, 1H, CH_{Ar}), 7.16 (ddd, ³*J* = 7.7 Hz, ³*J* = 7.0 Hz, ⁴*J* = 1.3 Hz, 1H, CH_{Ar}), 6.85 (s, 2H, CH_{Ar}), 6.61 (d, ⁴*J* = 2.5 Hz, 1H, CH_{thiophene}), 3.94 (s, 3H, CH₃), 3.89 (s, 6H, CH₃). ¹³C NMR (75 MHz, CDCl₃) δ = 154.2 (2C_{Ar}OCH₃), 148.1 (C_{Ar}), 146.3 (C_{Ar}), 136.5 (C_{Ar}), 135.1 (C_{Ar}), 133.4 (C_{Ar}), 126.6 (CH_{Ar}), 121.6 (CH_{Ar}), 120.4 (C_{Ar}), 120.0 (CH_{Ar}), 110.9 (CH_{Ar}), 110.0 (CH_{Ar}), 102.2 (2CH_{Ar}), 92.7 (CH_{Ar}), 61.2 (OCH₃), 56.5 (2OCH₃). IR (ATR, cm⁻¹): \tilde{v} = 3101 (m), 3056 (w), 2999 (m), 2929 (m), 2829

(w), 1592 (m), 1502 (m), 1450 (m), 1416 (m), 1354 (m), 1262 (m), 1226 (m), 1123 (s), 998 (m), 823 (m), 736 (s). MS (EI, 70 eV): m/z (%) = 339 (100), 324 (78), 296 (6), 280 (8), 238 (10), 210 (8), 172 (14). HRMS (EI): Calculated for $C_{19}H_{17}O_3NS$ [M]⁺ 339.09237 found 339.09241.

4-(Anthracen-2-yl)-4*H***-thieno[3,4-***b***]indole (6f): Light yellow solid, mp. 171 – 172 °C, 78% yield. ¹H NMR (250 MHz, Chloroform-***d***) \delta = 8.50 (s, 1H, CH_{Ar}), 8.44 (s, 1H, CH_{Ar}), 8.24 – 8.13 (m, 2H, CH_{Ar}), 8.11 – 7.96 (m, 2H, CH_{Ar}), 7.91 (ddd, ³***J* **= 7.5 Hz, ⁴***J* **= 1.3 Hz, ⁵***J* **= 0.7 Hz, 1H, CH_{Ar}), 7.79 (dd, ³***J* **= 9.0 Hz, ⁴***J* **= 2.1 Hz, 1H, CH_{Ar}), 7.59 – 7.44 (m, 4H, CH_{Ar}), 7.36 (ddd, ³***J* **= 8.3 Hz, ³***J* **= 7.3 Hz, ⁴***J* **= 1.3 Hz, 1H, CH_{Ar}), 7.20 (td, ³***J* **= 7.5 Hz, ⁴***J* **= 1.0 Hz, 1H, CH_{Ar}), 6.76 (d, ⁴***J* **= 2.5 Hz, 1H, CH_{thiophene}). ¹³C NMR (63 MHz, CDCl₃) \delta = 147.9 (C_{Ar}), 146.0 (C_{Ar}), 136.4 (C_{Ar}), 133.5 (C_{Ar}), 132.4 (C_{Ar}), 132.0 (C_{Ar}), 131.9 (C_{Ar}), 130.4 (CH_{Ar}), 130.1 (C_{Ar}), 128.4 (CH_{Ar}), 128.1 (CH_{Ar}), 126.7 (CH_{Ar}), 126.6 (CH_{Ar}), 126.1 (CH_{Ar}), 125.9 (CH_{Ar}), 125.7 (CH_{Ar}), 123.2 (CH_{Ar}), 121.6 (CH_{Ar}), 121.3 (CH_{Ar}), 120.7 (C_{Ar}), 120.3 (CH_{Ar}), 110.9 (CH_{Ar}), 110.2 (CH_{Ar}), 93.2 (CH_{Ar}). IR (ATR, cm⁻¹): \tilde{v} = 3093 (w), 3050 (w), 2956 (w), 1628 (w), 1573 (m), 1451 (m), 1389 (w), 1216 (w), 891 (m), 742 (s), 472 (m). MS (EI, 70 eV):** *m/z* **(%) = 349 (100), 304 (48), 174 (24), 152 (20), 128 (6). HRMS (EI): Calculated for C₂₄H₁₅NS [M]⁺ 349.09197 found 349.09161.**

General procedure for the synthesis of 5-substituted thieno[3,2-*b*]indoles

5-substituted 3-bromo-2-(2-bromophenyl)thiophene (0.15 mmol), amine (0.225 mmol), Pd₂dba₃ (0.0075 mmol), SPhos (0.015 mmol) and NaO*t*Bu (0.36 mmol) were added to a dried glass pressure tube. The tube was evacuated and backfilled three times with argon. 2 ml of dried toluene was added. The mixture was heated to 100 °C for 14h until the reaction completed (monitored by TLC). After cooling to room temperature, the solvent was removed under reduced pressure. The crude oil was subjected to column chromatography (heptane/ethyl acetate) to obtain the pure product.

2-Phenyl-4-(*p*-tolyl)-4*H*-thieno[3,2-*b*]indole (10a): White solid, mp. 164 – 165 °C, 95% yield. ¹H NMR (300 MHz, Chloroform-*d*) δ = 7.75 – 7.69 (m, 1H, CH_{Ar}), 7.65 – 7.58 (m, 2H, CH_{Ar}), 7.48 – 7.40 (m, 3H, CH_{Ar}), 7.37 – 7.29 (m, 4H, CH_{Ar}), 7.25 – 7.15 (m, 4H, CH_{Ar}), 2.42 (s, 3H, CH₃). ¹³C NMR (63 MHz, CDCl₃) δ = 145.9 (C_{Ar}), 145.4 (C_{Ar}), 141.1 (C_{Ar}), 137.0 (C_{Ar}), 136.3 (C_{Ar}), 135.5 (C_{Ar}), 130.5 (2CH_{Ar}), 129.1 (2CH_{Ar}), 127.7 (CH_{Ar}), 125.8 (2CH_{Ar}), 125.3 (2CH_{Ar}), 123.1 (CH_{Ar}), 122.5 (C_{Ar}), 120.4 (CH_{Ar}), 119.0 (CH_{Ar}), 116.9 (C_{Ar}), 111.1 (CH_{Ar}), 107.6 (CH_{Ar}), 21.3 (CH₃). IR (ATR, cm⁻¹): \tilde{v} = 3047 (m), 2916 (w), 1594 (m), 1512 (s), 1451 (s), 1421 (m), 1336 (m), 1211 (w), 1113 (w), 1068 (m), 917 (w), 827 (m), 802 (m), 755 (s), 727 (s), 689 (s), 619 (w), 574 (w). MS (EI, 70 eV): *m/z* (%) = 341 (8), 340 (26), 339 [M⁺]

(100), 338 (11), 324 (8), 323 (5), 170 (8), 162 (7), 146 (10). HRMS (EI): Calculated for $C_{23}H_{17}NS$ [M]⁺ 339.10762 found 339.10710.

2,4-Diphenyl-4*H***-thieno[3,2-***b***]indole (10b):** White solid, mp. 156 – 157 °C, 61% yield. ¹H NMR (250 MHz, Chloroform-*d*) δ = 7.84 – 7.69 (m, 2H, CH_{Ar}), 7.68 – 7.66 (m, 1H, CH_{Ar}), 7.48 – 7.34 (m, 5H, CH_{Ar}), 7.47 – 7.35 (m, 4H, CH_{Ar}), 7.33 – 7.23 (m, 3H, CH_{Ar}). ¹³C NMR (63 MHz, CDCl₃) δ = 146.0 (C_{Ar}), 145.2 (C_{Ar}), 141.0 (C_{Ar}), 138.9 (C_{Ar}), 135.4 (C_{Ar}), 130.0 (2CH_{Ar}), 129.1 (2CH_{Ar}), 127.8 (CH_{Ar}), 127.0 (CH_{Ar}), 125.8 (2CH_{Ar}), 125.4 (2CH_{Ar}), 123.2 (CH_{Ar}), 122.7 (C_{Ar}), 120.6 (CH_{Ar}), 119.1 (CH_{Ar}), 117.2 (C_{Ar}), 111.1 (CH_{Ar}), 107.6 (CH_{Ar}). IR (ATR, cm⁻¹): \tilde{v} = 3047 (w), 2921 (w), 1593 (m), 1526 (w), 1500 (s), 1450 (s), 1421 (m), 1342 (m), 1213 (w), 1069 (w), 819 (m), 752 (s), 741 (s), 691 (s), 663 (m), 615 (w). MS (EI, 70 eV): *m/z* (%) = 327 (6), 326 (24), 325 [M⁺] (100), 324 (22), 323 (7), 322(4), 291 (6), 146 (4). HRMS (EI): Calculated for C₂₂H₁₅NS [M]⁺ 325.09197 found 325.09163.

4-(4-Methoxyphenyl)-2-phenyl-4*H***-thieno[3,2-***b***]indole (10c): White solid, mp. 149 – 150 °C, 62% yield. ¹H NMR (250 MHz, Chloroform-***d***) \bar{\delta} = 7.80 – 7.73 (m, 1H, CH_{Ar}), 7.68 – 7.61 (m, 2H, CH_{Ar}), 7.48 (d, ³***J* **= 8.9 Hz, 2H, CH_{Ar}), 7.43 – 7.38 (m, 1H, CH_{Ar}), 7.35 (d, ³***J* **= 7.6 Hz, 2H, CH_{Ar}), 7.31 – 7.18 (m, 4H, CH_{Ar}), 7.07 (d, ³***J* **= 8.9 Hz, 2H, CH_{Ar}), 3.88 (s, 3H, OCH₃). ¹³C NMR (63 MHz, CDCl₃) \bar{\delta} = 158.6 (C_{Ar}), 145.9 (C_{Ar}), 145.7 (C_{Ar}), 141.5 (C_{Ar}), 135.5 (C_{Ar}), 131.6 (C_{Ar}), 129.1 (2CH_{Ar}), 127.7 (CH_{Ar}), 127.0 (2CH_{Ar}), 125.8 (2CH_{Ar}), 123.1 (C_{Ar}), 122.4 (CH_{Ar}), 120.3 (CH_{Ar}), 119.0 (CH_{Ar}), 116.6 (C_{Ar}), 115.1 (2CH_{Ar}), 110.9 (CH_{Ar}), 107.4 (CH_{Ar}), 55.7 (CH₃). IR (ATR, cm⁻¹): \tilde{v} = 2925 (w), 1509 (s), 1490 (m), 1451 (s), 1245 (s), 1212 (m), 1193 (m), 1179 (m), 1168 (m), 1151 (m), 1106 (m), 1070 (m), 1028 (s), 833 (m), 804 (m), 752 (s), 736 (s), 687 (s), 653 (w), 583 (s), 563 (w). MS (EI, 70 eV):** *m/z* **(%) = 357 (8), 356 (25), 355 [M]⁺ (100), 340 (13), 312 (9), 311 (4), 310 (6), 278 (4), 178 (4). HRMS (EI): Calculated for C₂₃H₁₇ONS [M]⁺ C₂₃H₁₇ONS 355.10254 found 355.10253.**

4-(4-Fluorophenyl)-2-phenyl-4*H***-thieno[3,2-***b***]indole (10d):** White solid, mp. 120 – 121 °C, 90% yield. ¹H NMR (250 MHz, Chloroform-*d*) δ = 7.83 – 7.75 (m, 1H, CH_{Ar}), 7.71 – 7.63 (m, 2H, CH_{Ar}), 7.63 – 7.52 (m, 2H, CH_{Ar}), 7.49 – 7.35 (m, 3H, CH_{Ar}), 7.34 – 7.23 (m, 6H, CH_{Ar}). ¹⁹F NMR (282 MHz, CDCl₃) δ = -114.40 (FC_{Ar}). ¹³C NMR (63 MHz, CDCl₃) δ = 161.41 (d, ¹*J*_{C-F} = 247.0 Hz, FC_{Ar}), 146.2 (C_{Ar}), 145.4 (C_{Ar}), 141.2 (C_{Ar}), 135.3 (C_{Ar}), 134.9 (d, ⁴*J*_{C-F} = 3.0 Hz, CF_{Ar}), 129.1 (2CH_{Ar}), 127.9 (CH_{Ar}), 127.3 (d, ³*J*_{C-F} = 8.5 Hz, 2CH_{Ar}), 125.8 (2CH_{Ar}), 123.3 (CH_{Ar}), 122.6 (C_{Ar}), 120.7 (CH_{Ar}), 119.1 (CH_{Ar}), 117.1 (C_{Ar}), 117.0 (d, ²*J*_{C-F} = 22.8 Hz, 2CH_{Ar}), 110.8 (CH_{Ar}), 107.2 (CH_{Ar}). IR (ATR, cm⁻¹): \tilde{v} = 3076 (w), 2923 (w), 1506 (s), 1451 (s), 1424 (m), 1342 (m), 1210 (s), 1149 (w), 1092 (m), 1069 (m), 1012 (w), 843 (s), 803 (s), 684 (s), 652 (w), 575 (m), 562 (m). MS (EI, 70 eV): *m/z* (%) = 345 (7), 344 (25), 343 [M]⁺ (100), 342 (20), 309 (7), 171 (6), 154 (7), 146 (4), 121 (4), 120 (6), 95 (4), 77 (4), 75 (7). HRMS (EI): Calculated for C₂₂H₁₄NFS [M]⁺ 343.08255 found 343.0823.

2-(4-Chlorophenyl)-4-(3,5-dimethylphenyl)-4*H***-thieno[3,2-***b***]indole (10e): White solid, mp. 105 – 106 °C, 62% yield. ¹H NMR (250 MHz, Chloroform-***d***) \delta = 7.78 – 7.70 (m, 1H, CH_{Ar}), 7.56 (d, ³***J* **= 8.6 Hz, 2H, CH_{Ar}), 7.52 – 7.46 (m, 1H, CH_{Ar}), 7.40 – 7.35 (m, 1H, CH_{Ar}), 7.32 (d, ³***J* **= 8.6 Hz, 2H, CH_{Ar}), 7.25 – 7.21 (m, 1H, CH_{Ar}), 7.20 – 7.13 (m, 3H, CH_{Ar}), 7.04 (m, 1H, CH_{Ar}), 2.41 (s, 6H, CH₃). ¹³C NMR (63 MHz, CDCl₃) \delta = 145.3 (C_{Ar}), 144.2 (C_{Ar}), 141.2 (C_{Ar}), 139.8 (2C_{Ar}), 138.6 (C_{Ar}), 134.0 (C_{Ar}), 133.4 (C_{Ar}), 129.2 (2CH_{Ar}), 128.9 (CH_{Ar}), 126.9 (2CH_{Ar}), 125.9 (C_{Ar}), 123.3 (CH_{Ar}), 123.1 (2CH_A), 122.4 (C_{Ar}), 120.5 (CH_{Ar}), 119.1 (CH_{Ar}), 111.3 (CH_{Ar}), 108.1 (CH_{Ar}), 21.6 (2CH₃). IR (ATR, cm⁻¹): \tilde{v} = 2916 (w), 2854 (w), 1595 (m), 1477 (m), 1451 (s), 1348 (m), 1314 (w), 1285 (w), 1169 (w), 1090 (m), 1011 (w), 828 (m), 801 (s), 737 (s), 703 (m), 687 (m), 672 (m), 551 (w). MS (EI, 70 eV):** *m/z* **(%) = 390 (11), 389 (42), 388 (31), 387 [M]⁺ (100), 372 (10), 193 (3), 168 (3). HRMS (EI): Calculated for C₂₄H₁₈NCIS [M]⁺ 387.08430 found 387.084213, calculated for C₂₄H₁₈N³⁷CIS [M]⁺ 389.08135 found 389.08135.**

4-(4-(*tert***-Butyl)phenyl)-2-(4-chlorophenyl)-4***H***-thieno[3,2-***b***]indole (10f): White solid, mp. 137 – 138 °C, 61% yield. ¹H NMR (250 MHz, Chloroform-***d***) δ = 7.75 – 7.69 (m, 1H, CH_{Ar}), 7.57 – 7.49 (m, 5H, CH_{Ar}), 7.49 – 7.43 (m, 3H, CH_{Ar}), 7.32 – 7.25 (m, 2H, CH_{Ar}), 7.23 – 7.16 (m, 2H, CH_{Ar}), 1.38 (s, 9H,** *t***Bu). ¹³C NMR (63 MHz, CDCl₃) δ = 150.1 (C_{Ar}), 145.3 (C_{Ar}), 144.3 (C_{Ar}), 141.1 (C_{Ar}), 136.0 (C_{Ar}), 134.0 (C_{Ar}), 133.3 (C_{Ar}), 129.2 (2CH_{Ar}), 126.9 (4CH_{Ar}), 124.9 (2CH_{Ar}), 123.3 (CH_{Ar}), 122.4 (C_{Ar}), 120.5 (CH_{Ar}), 119.1 (CH_{Ar}), 117.2 (C_{Ar}), 111.2 (CH_{Ar}), 108.0 (CH_{Ar}), 34.9 (C_{tBu}), 31.6 (3CH₃). IR (ATR, cm⁻¹): \tilde{v} = 2956 (m), 2902 (w), 1516 (m), 1487 (m), 1450 (s), 1361 (w), 1339 (w), 1261 (w), 1089 (s), 1012 (s), 834 (m), 802 (s), 791 (s), 746 (s), 672 (w), 628 (w), 551 (m). MS (EI, 70 eV):** *m/z* **(%) = 418 (11), 417 (39), 416 (28), 415 [M]⁺ (100), 402 (12), 401 (9), 400 (30), 385 (12), 186 (11). HRMS (EI): Calculated for C₂₆H₂₂NCIS [M]⁺ 415.11560 found 415.11531, calculated for C₂₆H₂₂N³⁷CIS [M]⁺ 417.11265 found 417.11365.**

2-(4-Chlorophenyl)-4-mesityl-4*H***-thieno[3,2-***b***]indole (10g): White solid, mp. 105 – 106 °C, 87% yield. ¹H NMR (250 MHz, Chloroform-***d***) \delta = 7.86 – 7.76 (m, 1H, CH_{Ar}), 7.57 (d, ³***J* **= 8.6 Hz, 2H, CH_{Ar}), 7.33 (d, ³***J* **= 8.6 Hz, 2H, CH_{Ar}), 7.28 – 7.20 (m, 2H, CH_{Ar}), 7.08 (s, 2H, CH_{Ar}), 7.00 – 6.92 (m, 2H, CH_{Ar}), 2.43 (s, 3H, CH₃), 1.91 (s, 6H, CH₃). ¹³C NMR (63 MHz, CDCl₃) \delta = 145.4 (C_{Ar}), 144.4 (C_{Ar}), 141.3 (C_{Ar}), 138.7 (C_{Ar}), 137.4 (2C_{Ar}), 134.1 (C_{Ar}), 133.3 (C_{Ar}), 132.9 (C_{Ar}), 129.4 (2CH_{Ar}), 129.2 (2CH_{Ar}), 126.8 (2CH_{Ar}), 123.2 (CH_{Ar}), 121.9 (C_{Ar}), 120.0 (CH_{Ar}), 119.1 (CH_{Ar}), 116.2 (C_{Ar}), 110.9 (CH_{Ar}), 107.4 (CH_{Ar}), 21.3 (CH₃), 17.7 (2CH₃). IR (ATR, cm⁻¹): \tilde{v} = 2950 (w), 2916 (w), 1603 (w), 1501 (s), 1484 (s), 1450 (m), 1314 (m), 1213 (w), 1179 (w), 1010 (w), 852 (w), 827 (m), 800 (s), 739 (s), 677 (w), 552 (w). MS (EI, 70 eV):** *m/z* **(%) = 404 (11), 403 (38), 402 (29), 401 [M]⁺ (100), 386 (4), 368 (3), 247 (3), 232 (3), 231 (3). HRMS (EI): Calculated for C₂₅H₂₀NCIS [M]⁺ 401.09995 found 401.09960, calculated for C₂₅H₂₀N³⁷CIS [M]⁺ 403.09700 found: 403.09786.**

4-(3-Fluorophenyl)-2-(4-fluorophenyl)-4*H*-thieno[3,2-*b*]indole (10h): White solid, mp. 156 – 157 °C, 62% yield. ¹H NMR (250 MHz, Chloroform-d) δ = 7.80 – 7.73 (m, 1H, CH_{Ar}), 7.66 – 7.58 (m, 2H, CH_{Ar}), 7.58 – 7.48 (m, 2H, CH_{Ar}), 7.41 (ddd, ³J = 8.0 Hz, ⁴J = 2.0 Hz, ${}^{5}J = 1.1$ Hz, 1H, CH_{Ar}), 7.37 – 7.30 (m, 1H, CH_{Ar}), 7.30 – 7.20 (m, 3H, CH_{Ar}), 7.16 – 7.03 (m, 3H, CH_{Ar}). ¹⁹F NMR (235 MHz, CDCl₃) δ = -110.36 (FC_{Ar}), -114.04 (FC_{Ar}). ¹³C NMR (63 MHz, CDCl₃) δ = 163.5 (d, ¹J_{C-F} = 248.1 Hz, CF_{Ar}), 162.6 (d, ¹J_{C-F} = 247.9 Hz, CF_{Ar}), 146.0 (C_{Ar}) , 145.1 (C_{Ar}) , 140.6 (C_{Ar}) , 140.4 $(d, {}^{3}J_{C-F} = 10.0 \text{ Hz}, C_{Ar})$, 131.6 $(d, {}^{4}J_{C-F} = 3.5 \text{ Hz}, C_{Ar})$, 131.1 (d, ${}^{3}J_{C-F} = 9.2$ Hz, CH_{Ar}), 127.4 (d, ${}^{3}J_{C-F} = 8.0$ Hz, 2CH_{Ar}), 123.5 (CH_{Ar}), 122.8 (C_{Ar}), 121.1 (CH_{Ar}), 120.6 (d, ${}^{4}J_{C-F}$ = 3.2 Hz, CH_{Ar}), 119.2 (CH_{Ar}), 117.7 (C_{Ar}), 116.0 (d, ${}^{2}J_{C-F}$ = 21.9 Hz, 2CH_{Ar}), 113.8 (d, ${}^{2}J_{C-F} = 21.1$ Hz, CH_{Ar}), 112.4 (d, ${}^{2}J_{C-F} = 23.4$ Hz, CH_{Ar}), 111.0 (CH_{Ar}), 107.5 (CH_{Ar}). IR (ATR, cm⁻¹): \tilde{v} = 3052 (w), 1592 (m), 1531 (m), 1490 (s), 1452 (m), 1364 (w), 1261 (w), 1222 (s), 1145 (s), 1080 (w), 977 (w), 934 (w), 870 (w), 828 (m), 806 (s), 777 (m), 725 (s), 708 (m), 694 (s), 667 (s), 630 (w), 581 (w). MS (EI, 70 eV): m/z (%) = 363 (7), 361 [M]⁺ (100), 360 (21), 359 (6), 266 (4). HRMS (EI): Calculated for C₂₂H₁₃NF₂S [M]⁺ 361.07313 found 361.07251.

4-(4-(*tert***-Butyl)phenyl)-2-(4-fluorophenyl)-4***H***-thieno[3,2-***b***]indole (10i): White solid, mp. 118 – 119 °C, 85% yield. ¹H NMR (300 MHz, Chloroform-***d***) δ = 7.72 – 7.67 (m, 1H, CH_{Ar}), 7.59 – 7.41 (m, 7H, CH_{Ar}), 7.20 – 7.15 (m, 3H, CH_{Ar}), 7.04 – 6.95 (m, 2H, CH_{Ar}), 1.34 (s, 9H,** *t***Bu). ¹³C NMR (75 MHz, CDCl₃) δ = 162.6 (d, ¹J_{C-F} = 247.5 Hz, CF_{Ar}), 150.1 (C_{Ar}), 145.3 (C_{Ar}), 144.6 (C_{Ar}), 141.1 (C_{Ar}), 136.1 (C_{Ar}), 131.9 (d, ⁴J_{C-F} = 3.3 Hz, C_{Ar}), 127.5 (d, ³J_{C-F} = 8.0 Hz, 2CH_{Ar}), 126.8 (2CH_{Ar}), 124.9 (2CH_{Ar}), 123.2 (CH_{Ar}), 122.6 (C_{Ar}), 120.5 (CH_{Ar}), 119.0 (CH_{Ar}), 116.9 (C_{Ar}), 116.1 (d, ²J_{C-F} = 21.9 Hz, 2CH_{Ar}), 111.2 (CH_{Ar}), 107.8 (CH_{Ar}), 34.9 (C_{***t***Bu}), 31.6 (3CH₃). IR (ATR, cm⁻¹): \tilde{v} = 2963 (w), 1602 (w), 1497 (m), 1451 (m), 1361 (w), 1342 (w), 1213 (s), 1159 (m), 1096 (w), 1013 (w), 840 (s), 804 (s), 787 (m), 738 (s), 674 (m), 633 (w), 552 (s). MS (EI, 70 eV):** *m/z* **(%) = 401 (8), 400 (29), 399 [M]⁺ (100), 385 (10), 384 (35), 369 (16), 342 (9), 266 (10), 192 (8), 178 (26). HRMS (EI): Calculated for C₂₆H₂₂NFS [M]⁺ 399.14515 found 399.14496.**

2-(4-(*tert***-Butyl)phenyl)-4-mesityl-4***H***-thieno[3,2-***b***]indole (10j): White solid, mp. 181 – 182 °C, 45% yield. ¹H NMR (250 MHz, Chloroform-***d***) \delta = 7.83 – 7.76 (m, 1H, CH_{Ar}), 7.58 (d, ³***J* **= 8.6 Hz, 2H, CH_{Ar}), 7.39 (d, ³***J* **= 8.6 Hz, 2H, CH_{Ar}), 7.20 (m, 2H, CH_{Ar}), 7.07 (s, 2H, CH_{Ar}), 6.96 (s, 1H, CH_{thiophene}), 6.95 – 6.90 (m, 1H, CH_{Ar}), 2.42 (s, 3H, CH₃), 1.91 (s, 6H, CH₃), 1.34 (s, 9H,** *t***Bu). ¹³C NMR (63 MHz, CDCl₃) \delta = 150.8 (C_{Ar}), 146.1 (C_{Ar}), 145.5 (C_{Ar}), 141.2 (C_{Ar}), 138.6 (C_{Ar}), 137.5 (2C_{Ar}), 133.1 (C_{Ar}), 132.8 (C_{Ar}), 129.4 (2CH_{Ar}), 126.0 (2CH_{Ar}), 125.4 (2CH_{Ar}), 122.8 (CH_{Ar}), 122.1 (C_{Ar}), 119.8 (CH_{Ar}), 118.9 (CH_{Ar}), 115.5 (C_{Ar}), 110.8 (CH_{Ar}), 106.7 (CH_{Ar}), 34.8 (C_{tBu}), 31.4 (3CH₃), 21.3 (CH₃), 17.7 (2CH₃). IR (ATR, cm⁻¹): \tilde{\nu} = 2957 (w), 2921 (w), 1502 (m), 1484 (m), 1452 (m), 1357 (w), 1335 (w), 1218 (w), 937 (w), 836 (m), 807 (s), 743 (s), 574 (w), 531 (m). MS (EI, 70 eV):** *m/z* **(%) = 425 (7), 424 (31), 423**

$$\label{eq:main_select} \begin{split} [M]^+ \ (100), \ 410 \ (4), \ 409 \ (13), \ 408 \ (45), \ 393 \ (10), \ 204 \ (4), \ 190 \ (5). \ HRMS \ (EI): \ Calculated \ for \\ C_{29}H_{29}NS \ [M]^+ \ 423.20152 \ found \ 423.20115. \end{split}$$

Acknowledgement

Scholarship for N.N.P. by the DAAD is gratefully acknowledged.

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