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Photoacid generation from substituted benzo[*b*]thiophene-2-carboxanilides

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Experimental

^{1}H and ^{13}C NMR spectra were recorded on Bruker DRX-400 (400, 126 MHz) and AVANCE-500 (500, 126 and 471 MHz) spectrometers. The internal standard for ^{1}H NMR was tetramethylsilane, for ^{13}C NMR – signals of the deuterated solvent $CDCl_3$ (δ_C = 77.0 ppm) or DMSO-d_6 (δ_C = 39.5 ppm). High-resolution mass spectrometry was performed using a Bruker maXis Impact HD spectrometer. Infrared spectra were recorded on a Spectrum Two spectrometer.[S1] Absorption and fluorescence spectra were recorded on a CM-2203 spectrophotometer (SOLAR, Belarus).[S1] An Nd:YAG laser LQ529B (SOLAR LS, Belarus) was used for photolysis.

Compound **5**, synthesized using our previous method, was used as an acid-base indicator [S2].

Solutions of compounds **1-4** in toluene (2 ml) at a concentration of 10^{-4} M in a quartz cuvette were subjected to fractional irradiation with 10 pulses of the 3rd laser harmonic (355 nm, 40 mJ/pulse, 200 mJ/cm^2) with the subsequent recording of the absorption spectra. To detect the acid produced during photolysis, a solution of 4,6-bis[5-(9-ethyl-9*H*-carbazol-3-yl)thiophen-2-yl]pyrimidine (**5**) in toluene was prepared and added to the solution containing the compounds under investigation, achieving an **5** concentration of 10^{-5} M.

The quantum yield of the compounds' phototransformation was calculated using the following equation S1:

$$\gamma = \frac{N_{ph}}{N_{abs}}, \quad \text{(S1)}$$

where N_{ph} is the number of molecules that undergo phototransformation, and N_{abs} is the number of photons absorbed by the compound during a certain number of pulses. N_{ph} was determined by the decrease in the intensity of the main band maximum after n irradiation pulses using the equation S2

$$N_{ph} = \frac{(D_0 - D_n) \times C_0 N V}{D_0 \times 10^3}, \quad \text{(S2)}$$

where D_0 and D_n are the optical densities of the solution before and after n irradiation pulses, C_0 is the initial concentration (in mol/L), N is Avogadro constant, and V is the irradiated volume (in mL). In the case of laser irradiation, energy in the E_p pulse (40 mJ in our case) can be easily calculated using the number of photons absorbed, taking into account transmission coefficient $T = 10^{-D_{355}}$ of the solution at the excitation wavelength 355 nm and photon energy $E_{h\nu}$ of $5{,}6\times10^{-19}$ J, then:

$$N_{abs} = \frac{nE_p \times (1-T)}{E_{h\nu}} \quad \text{(S3)}$$

By analogy with expression S1, the efficiency of formation of the protonated form φ of compound **5**, acting as an indicator, was estimated. The number of molecules of **5** protonated by the acid formed by photogenerators in 10 irradiation pulses was taken as N_{Ph}. N_{Ph} was calculated from the drop in optical density in the band of the neutral form (412 nm).

The values of γ and φ differ, since γ characterizes the degree of phototransformation of PAG, and φ determines how much the indicator reacts with the acid. A certain level of acidity must be reached for the indicator to begin to react with the acid, so the φ value will be lower than γ.

Absorption spectra of compound 5 in the presence of dichloroacetic acid

To confirm the properties of the **5** as an indicator, it was titrated in toluene with dichloroacetic acid (DCA), which was also dissolved in toluene. As shown in Figure S1a, the gradual addition of dichloroacetic acid to the **5** solution shifts the absorption band from 412 nm to 530 nm. This shift indicates the conversion of the compound from a neutral to a protonated form, resulting in a crimson color in the solution.

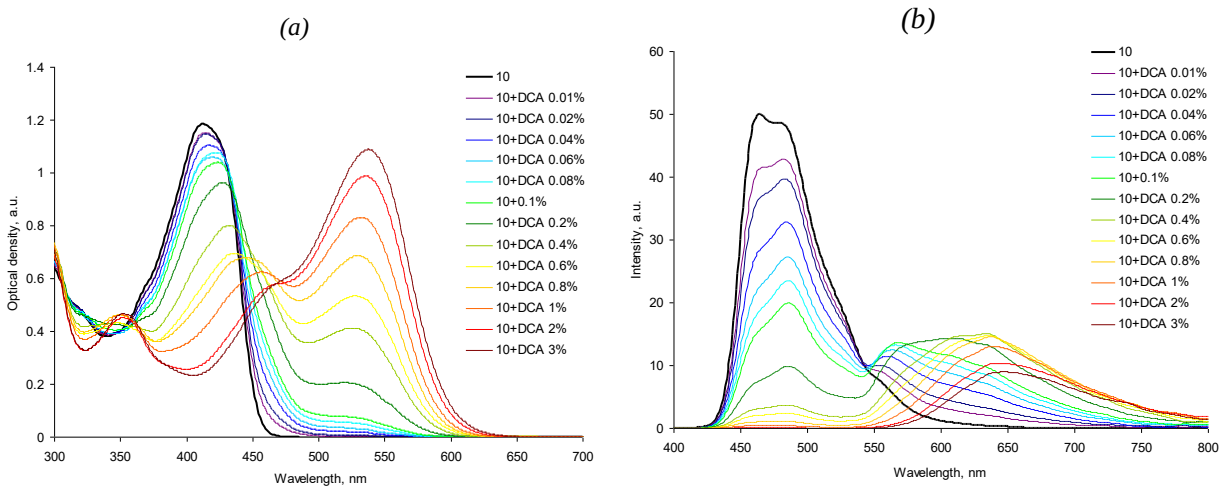
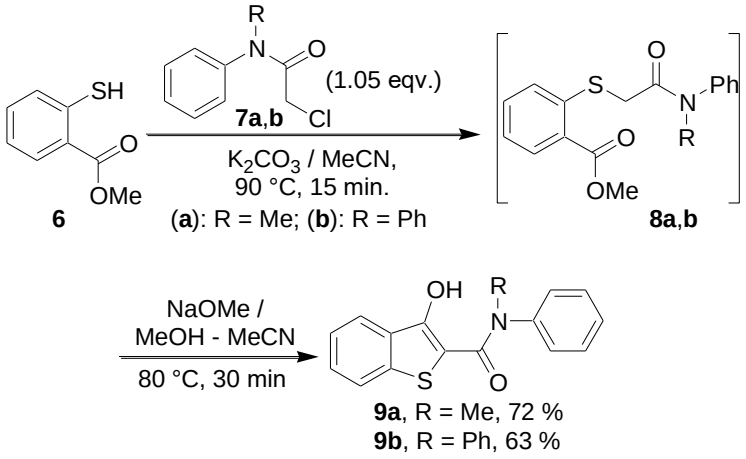


Figure S1 – Titration of **10** with dichloroacetic acid in toluene: (*a*) absorption and (*b*) fluorescence

The expected isosbestic point is not observed during titration of **5** with dichloroacetic acid in toluene. We see two possible reasons for this. Firstly, in some cases acid-base reactions proceed not through the formation of an isosbestic point, but with a lateral or vertical shift, as is well illustrated in [S1]. Secondly, our indicator has two possible protonation centers, two nitrogen atoms in the bipyridine ring. It is possible that at a certain concentration of acid, protonation of the second nitrogen atom is activated, which will certainly affect the absence of an obvious isosbestic point. At high acid concentrations the absorption band is not smooth; in addition to the maximum at 530 nm there is a shoulder at 470 nm. Perhaps the second reason is more likely. In the fluorescence spectra (Figure S1b), the addition of acid results in a drop in the band at 480 nm and the appearance of a broad band with a maximum first at 570 nm and then a shift of its maximum to 647 nm. This shift also indicates two protonation centers.

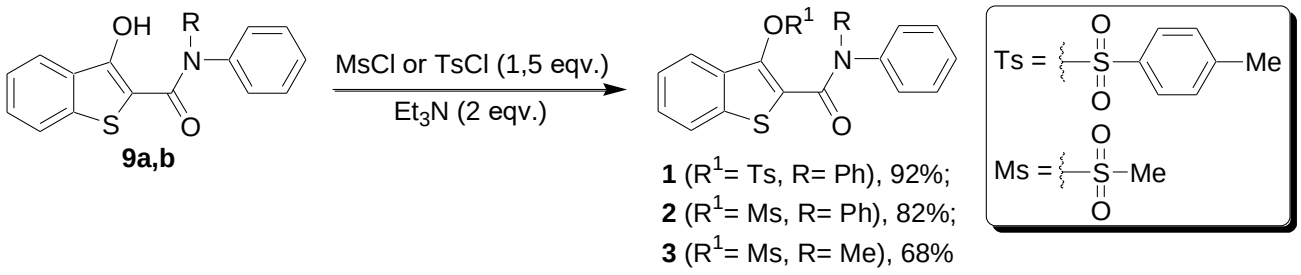
Synthesis of 3-substituted benzo[*b*]thiophene-2-carboxanilides 1-4

Compounds **1-3** were synthesized starting from methyl thiosalicylate **6**. For this purpose, 3-hydroxybenzo[*b*]thiophene-2-carboxamides **9a,b** were prepared by S-alkylation of thiosalicylate **6** with chloroacetamides **7a,b**, using potassium carbonate in an acetonitrile solution. The intermediate 2-sulfenyl substituted benzoates **8a,b** were not isolated. Instead, they were directly cyclized by treatment with sodium methoxide in methanol to yield products **9a,b** (Scheme S1).



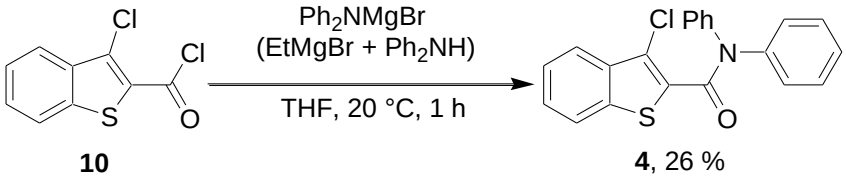
Scheme S1

Next, *O*-mesylation and *O*-tosylation of 3-hydroxybenzo[*b*]thiophene-2-carboxamides **9a,b** were performed by their reaction with mesyl chloride (MsCl) or tosyl chloride (TsCl) in the presence of triethylamine to obtain the target 3-mesyloxy- and 3-tosyloxy-substituted benzo[*b*]thiophene-2-carboxaanilides (Scheme S2).



Scheme S2

In turn, compound **4** was synthesized by the reaction of acid chloride **10** [S3] with (diphenylamido)magnesium bromide, which was obtained in situ from diphenylamine and ethylmagnesium bromide in a solution of dry THF (Scheme S3). It has been established that the reaction of substrate **10** with diphenylamine does not occur in the presence of triethylamine due to its insufficient nucleophilicity.



Scheme S3

General procedure for the synthesis of 3-hydroxybenzo[*b*]thiophene-2-carboxamides (9a,b).
K_2CO_3 powder (4.14 g, 30 mmol) was added to a solution of thiosalicylate **6** (3.36 g, 20 mmol) and chloroacetamide **7a** (3.86 g, 21 mmol) or **7b** (5.17 g, 21 mmol) in acetonitrile (50 mL), and the mixture was stirred and heated at 90 °C for 15 min, and then the precipitated inorganic salts were filtered off. A solution of NaOMe prepared from metallic Na (0.69 g, 30 mmol) and methanol (15 mL) was added to the filtrate, and the mixture was stirred and heated at 80 °C for 30 min. After the solution began to boil, a bright yellow sodium salt of **9** precipitated. Dichloromethane (20 mL), acetic acid (1.7 mL, 30 mmol) and water (300 mL) were added to the resulting suspension. The organic phase was separated, concentrated and the solid residue was purified by crystallization from ethanol.

3-Hydroxy-N-methyl-N-phenylbenzo[b]thiophene-2-carboxamide **9a***:* Cream crystals, yield 4.12 g (72 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 13.21 (s, 1H), 7.90 (dd, J1 = 7.1, J2 = 1.3 Hz, 1H), 7.56–7.47 (m, 3H), 7.44–7.39 (m, 1H), 7.38–7.27 (m, 4H), 3.45 (s, 3H).

3-Hydroxy-N,N'-diphenylbenzo[b]thiophene-2-carboxamide **9b***:* Cream crystals, yield 4.3 g (63 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.95 (s, 1H), 7.93 (dd, J1 = 7,4, J2 = 0,9 Hz, 1H), 7.49–7.29 (m, 13H).

General procedure for the synthesis of 3-mesyloxybenzo[*b*]thiophene-2-carboxanilides 2 and 3.
Triethylamine (0.55 mL, 4 mmol) was added dropwise to a solution of substrate **9a** (572 mg, 2 mmol) or **9b** (700 mg, 2 mmol) and methanesulfonyl chloride (0.24 mL, 3 mmol) in $CHCl_3$ (20 mL) while ice cooling to 0–5 °C and the resulting mixture was kept for 1 h. Water (100 ml) and hydrochloric acid (2 mL, 37 % wt.) were then added, and the mixture was extracted with chloroform (2×10 mL). The extract was concentrated, and the resulting semi-solid residue was purified by crystallization from methanol.

Synthesis of 3-tosyloxybenzo[*b*]thiophene-2-carboxamide (1).
Triethylamine (0.55 mL, 4 mmol) was added to a solution of substrate **9a** (572 mg, 2 mmol) and 4-toluenesulfonyl chloride (570 mg, 3 mmol) in anhydrous pyridine (5 mL) while ice cooling to 0–5 °C and the resulting mixture was heated to reflux at 120 °C for 10 min. Water (100 mL) and hydrochloric acid (2 mL, 37 % wt.) were added to the reaction mixture, and it was extracted with $CHCl_3$ (2×10 mL). The organic extract was concentrated, and the resulting residue was purified by crystallization from ethanol.

2-(Diphenylcarbamoyl)benzo[b]thiophen-3-yl tosylate **1***:* Colorless microcrystals, yield 930 mg (92 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7,76 (d, J = 8.3 Hz, 2H), 7,64 (d, J = 8.2 Hz, 2H), 7.36–7.26 (m, 9H), 7,21 (dd, J1 = 12.9, J2 = 6.9 Hz, 4H), 7.12–7.06 (m, 1H), 7.02 (d, J = 8.1 Hz, 1H), 2.38 (c, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.0, 145.8, 142.6, 136.6, 136.2, 132.2, 131.5, 129.8, 128.9, 128.5, 128.5, 127.4, 126.8, 126.5, 124.6, 122.4, 121.7, 21.6. IR, ν, cm^{-1}: 461, 499, 543, 575, 613, 653 626, 693 676, 716 725 750 740, 764, 799 809 832, 886, 907, 958, 1013, 1030, 1075 1059, 1089, 1180, 1192, 1257, 1300, 1334, 1357, 1375, 1435, 1451, 1491, 1531, 1567, 1592, 1643, 3063. HRMS (ESI) calcd for $C_{28}H_{22}NO_4S_2^+$ 500.0985 $[M+H]^+$, found m/z 500,0992 $[M+H]^+$.

2-(Diphenylcarbamoyl)benzo[b]thiophen-3-yl methanesulfonate **2**: Cream crystals, yield 700 mg (82 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.79 (m, 1H), 7.66–7.60 (m, 1H), 7.44–7.37 (m, 2H), 7.36–7.28 (m, 8H), 7.27–7.21 (m, 2H), 3.36 (s, 3H). ^{13}C NMR (126

MHz, CDCl3) δ 162.0, 142.6, 138.6, 137.0, 131.6, 129.2, 127.5, 127.14, 127.10, 126.3, 125.3, 122.5, 122.3, 39.0. IR, ν, cm^{-1}: 436, 462, 499, 515, 527, 571, 619, 610, 624, 671, 694, 712, 721, 748, 736, 758, 768, 806, 889, 906, 969, 990, 1003,1033,1025, 1058, 1076, 1102, 1140, 1164, 1182, 1255, 1301, 1338, 1357, 1417, 1434, 1454, 1493, 1531, 1570, 1591, 1651, 2933, 3011, 3034, 3065. HRMS (ESI) calcd for $C_{22}H_{18}NO_4S_2^+$ 424.0672 $[M+H]^+$, found m/z 424.0670 $[M+H]^+$.

*2-(N-Methyl-N-phenylcarbamoyl)benzo[b]thiophen-3-yl methanesulfonate***3**: Cream crystals, yield 490 mg (68 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.79 (m, 1H), 7.62–7.56 (m, 1H), 7.42–7.33 (m, 2H), 7.33–7.21 (m, 5H), 3.49 (s, 3H), 3.40 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.9, 143.1, 138.2, 136.8, 131.6, 129.3, 127.7, 126.9, 126.8, 125.5, 125.2, 122.3, 38.8, 38.3 (one signal ($1C_{Ar}$) was not identified due to peeks overlapping). IR, ν, cm^{-1}: 420, 439, 503, 527, 513, 556, 567, 617, 690, 716, 743, 730, 769, 794, 808, 832, 901, 968, 1014, 1034, 1100, 1134, 1175, 1183, 1256, 1282, 1298, 1366, 1354, 1402, 1417, 1464, 1496, 1512, 1566, 1594, 1636, 2940, 3021, 3039. HRMS (ESI) calcd for $C_{17}H_{16}NO_4S_2^+$ 362.0520 $[M+H]^+$, found m/z 362,0520 $[M+H]^+$.

Procedure for the synthesis of 3-chloro-*N*,*N*-diphenylbenzo[*b*]thiophene-2-carboxamide (4)

A solution of diphenylamine (1.69 g, 10 mmol) in dry THF (5 mL) was added to a Grignard reagent prepared from ethyl bromide (1.1 g, 10 mmol) and metallic magnesium (0.24 g, 10 mmol) in dry THF (30 mL) under an argon atmosphere, and this was stirred for 30 min. The obtained solution was added dropwise to a stirred solution of 3-chlorobenzo[*b*]thiophene-2-carbonyl chloride **10** (1.6 g, 7 mmol) under ice cooling. The reaction mixture was kept for 1 h, poured into ice-cold water (400 mL) with hydrochloric acid (1 mL, 37 % wt.), and extracted with dichloromethane (2×20 mL). The organic extract was concentrated at atmospheric pressure, and the residue was crystallized from n-butyl acetate (10 mL).

3-Chloro-N,N-diphenylbenzo[b]thiophene-2-carboxamide **4**: Light yellow crystals, yield 660 mg (26 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.67 (m, 2H), 7.43–7.37 (m, 2H), 7.35–7.26 (m, 8H), 7.24–7.17 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162,9, 142,4, 137,9, 135,6, 131,4, 129,0, 127,2, 127,0, 126,6, 125,1, 122,7, 122,5, 121,3. IR, ν, cm^{-1}: 413, 444, 456, 500, 529, 586, 614, 632, 690, 698, 722, 750, 792, 827, 852, 912, 932, 958, 1003, 1027, 1077, 1160, 1174, 1250, 1269, 1305, 1320, 1344, 1431, 1458, 1489, 1516, 1593, 1650, 3010, 3063, 3089, 3291. HRMS (ESI) calcd for $C_{21}H_{15}ClNOS^+$ 364.0557 $[M+H]^+$, found m/z 364.0557 $[M+H]^+$.

References

S1 J. Ya. Bershtein and Yu. L. Kaminsky, *Spectrophotometric Analysis in Organic Chemistry*, Khimiia, 1975 (in Russian).

S2 E. M. Dinastiya, E. V. Verbitskiy, R. M. Gadirov, L. G. Samsonova, K. M. Degtyarenko, D. V. Grigoryev, A. E. Kurtcevich, T. A. Solodova, E. N. Tel'minov, G. L. Rusinov, O. N. Chupakhin and V. N. Charushin, *J. Photochem. Photobiol., A*, 2021, **408**, 113089; https://doi.org/10.1016/j.jphotochem.2020.113089.

S3 W. Ried, G. Oremek and B. Ocakcioglu, *Liebigs Ann. Chem*., 1980, **9**, 1424; https://doi.org/10.1002/JLAC.198019800911.

NMR Spectra

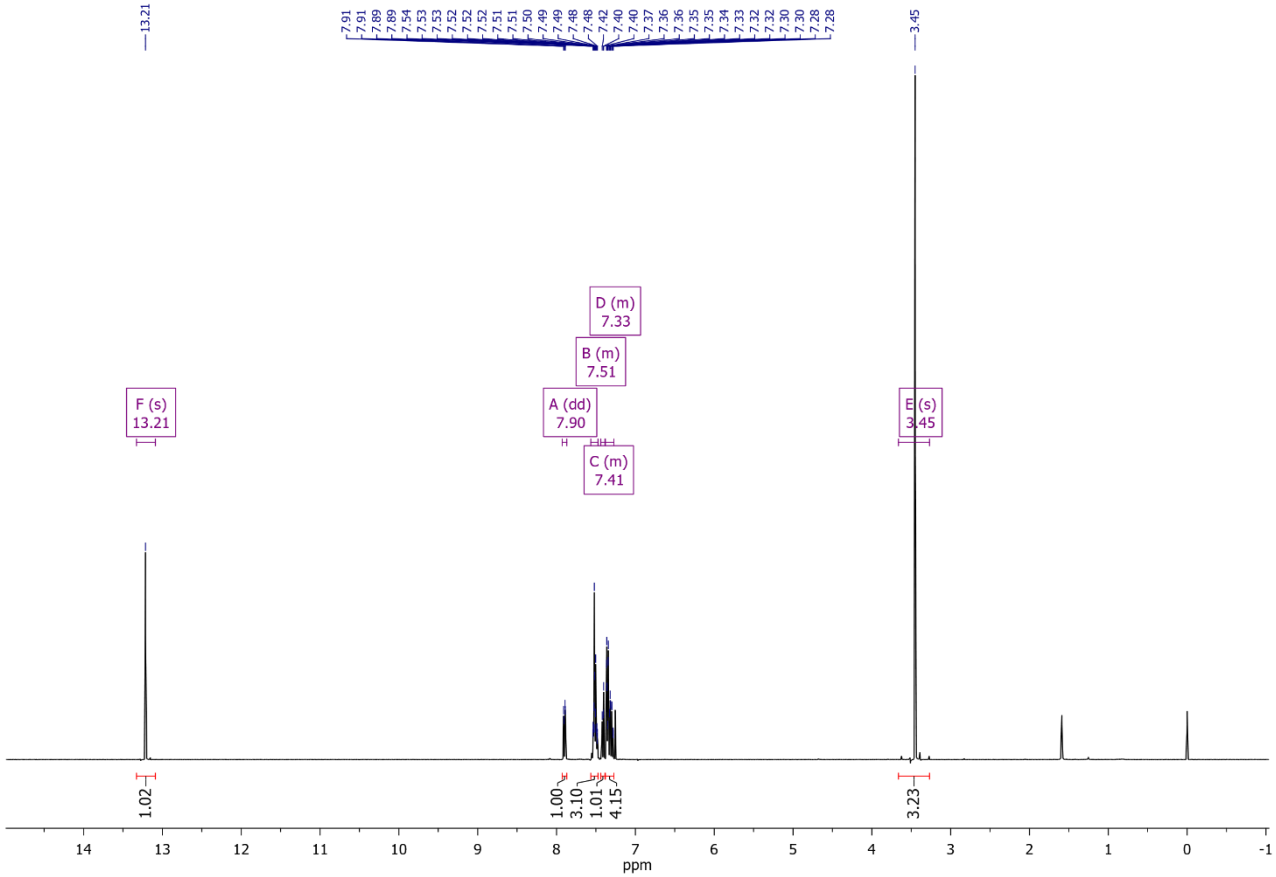


Figure S2. [1]H NMR spectrum of 3-hydroxy-*N*-methyl-*N*-phenylbenzo[*b*]thiophene-2-carboxamide (**9a**)

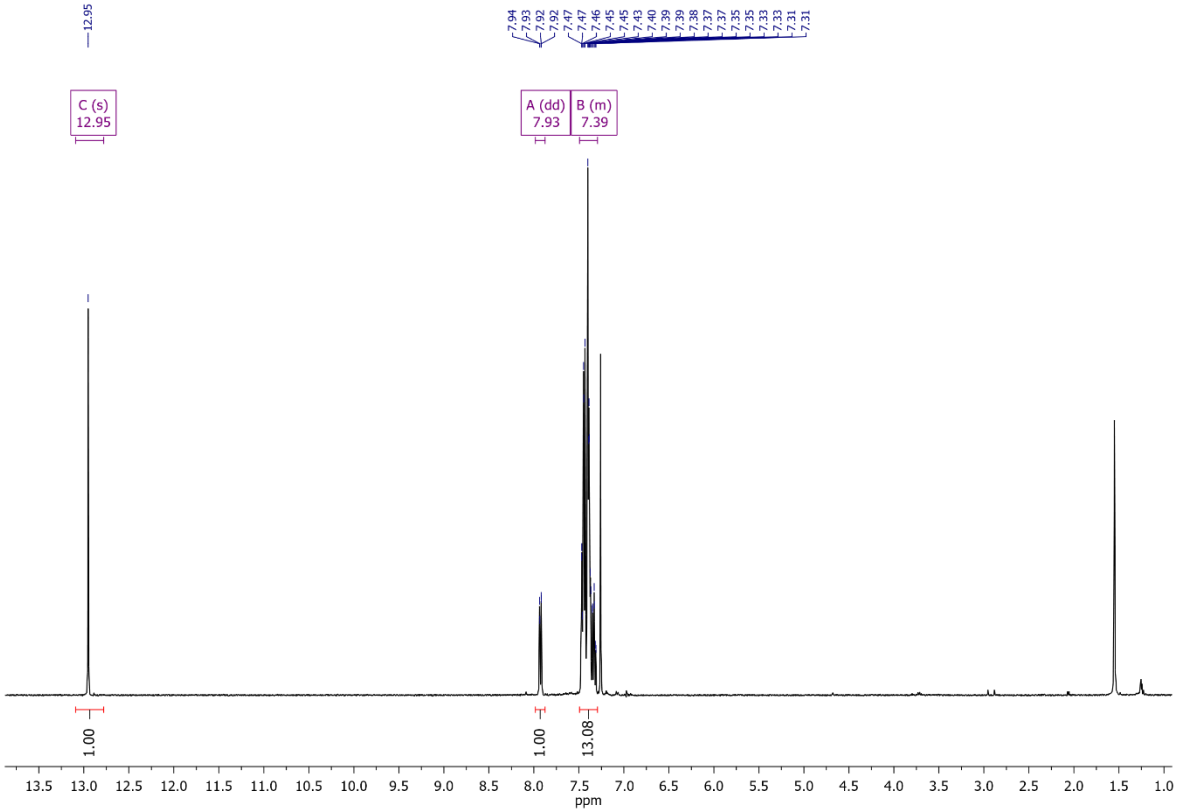


Figure S3. [1]H NMR spectrum of 3-hydroxy-*N*,*N*-diphenylbenzo[*b*]thiophene-2-carboxamide (**9b**).

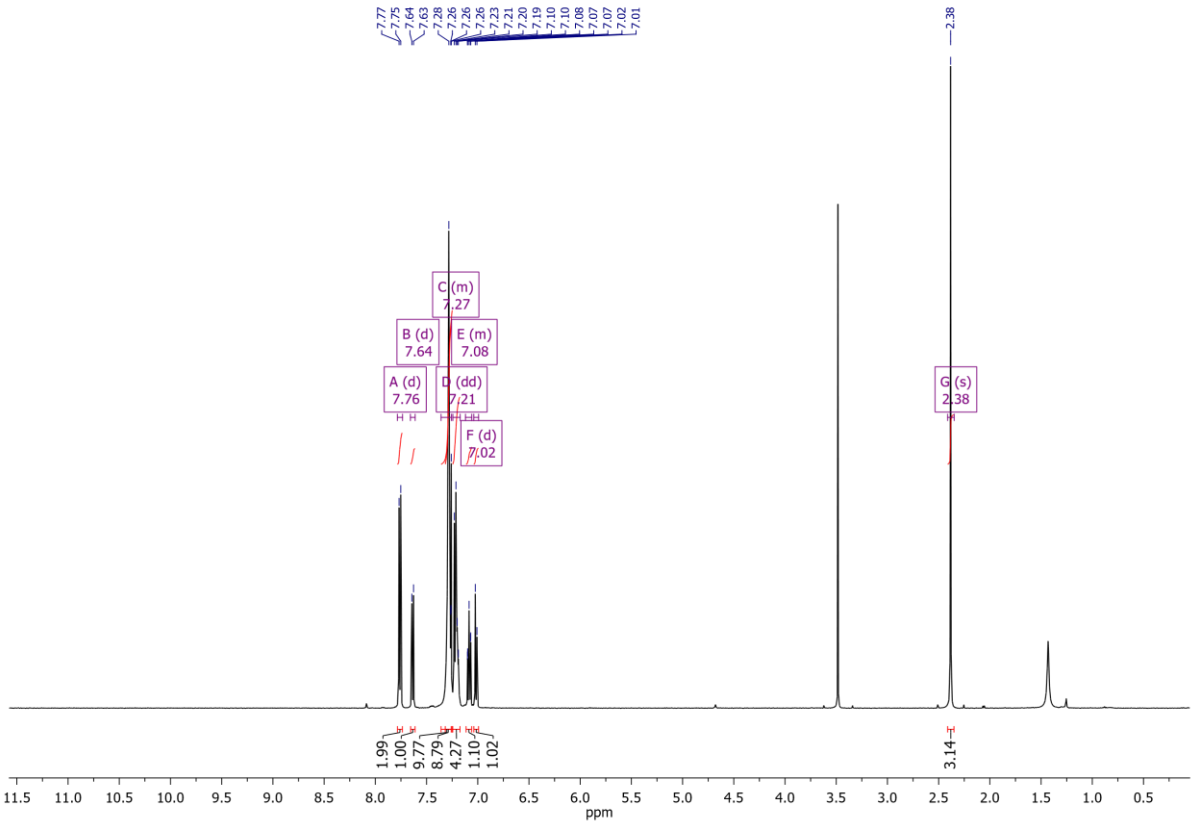


Figure S4. [1]H NMR spectrum of 2-(diphenylcarbamoyl)benzo[*b*]thiophen-3-yl 4-methylbenzenesulfonate (**1**).

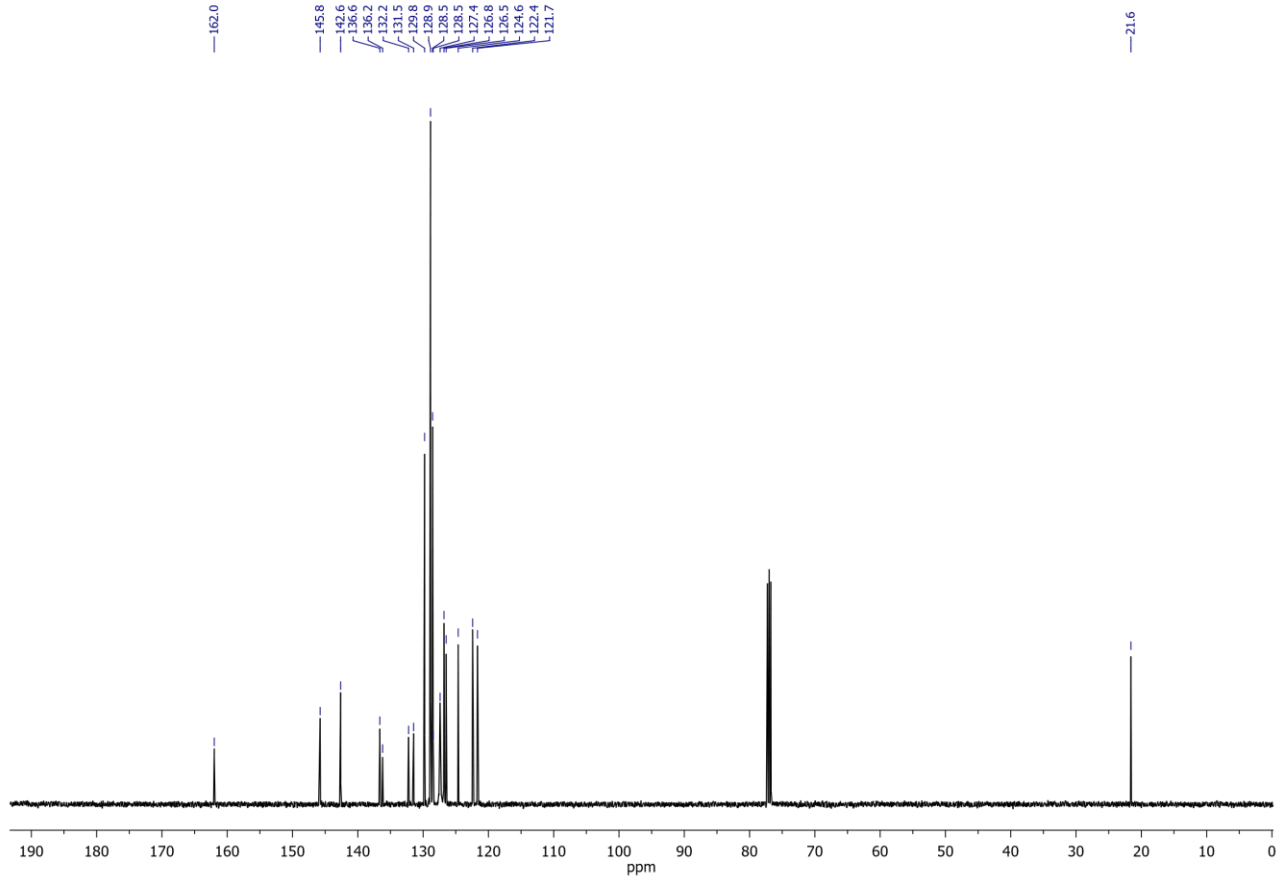


Figure S5. [13]C NMR spectrum of 2-(diphenylcarbamoyl)benzo[*b*]thiophen-3-yl 4-methylbenzenesulfonate (**1**).

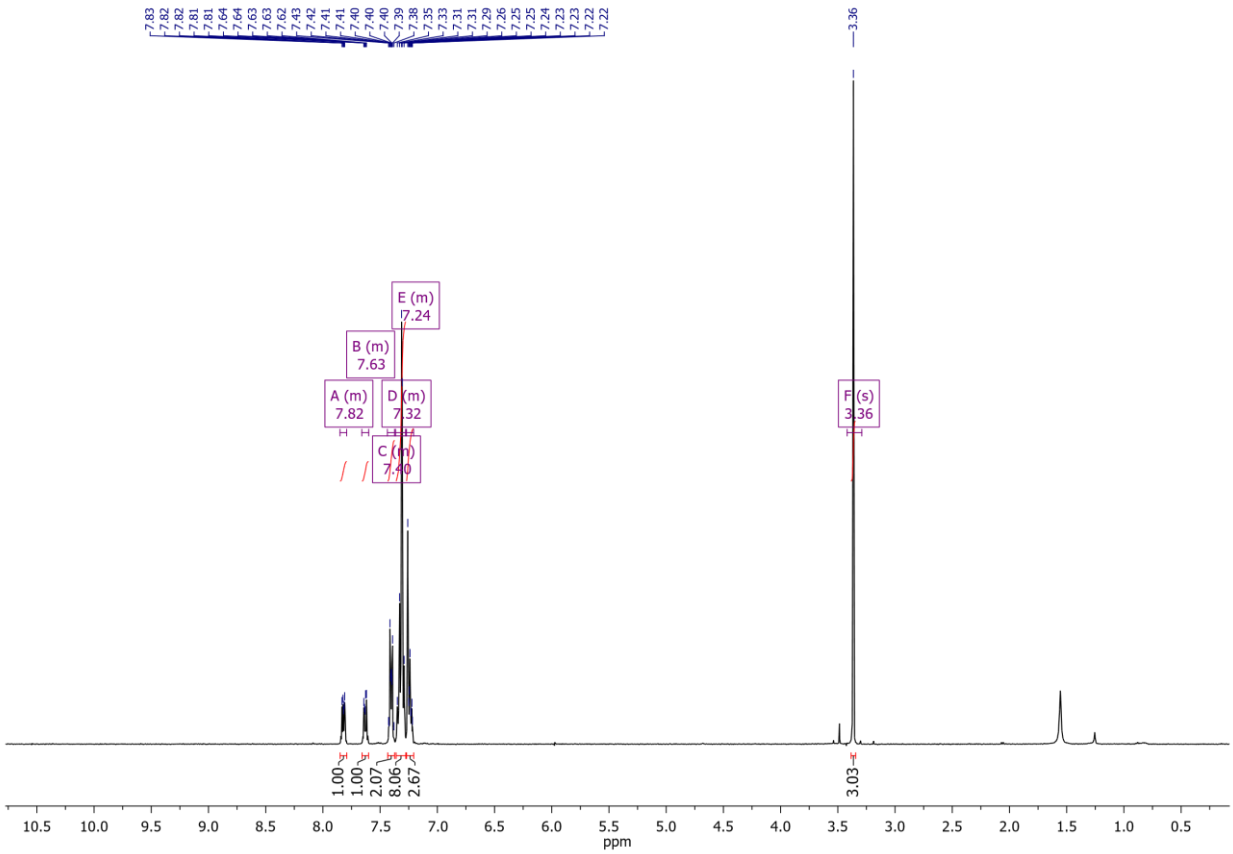


Figure S6. [1]H NMR spectrum of 2-(diphenylcarbamoyl)benzo[*b*]thiophen-3-yl methanesulfonate (**2**).

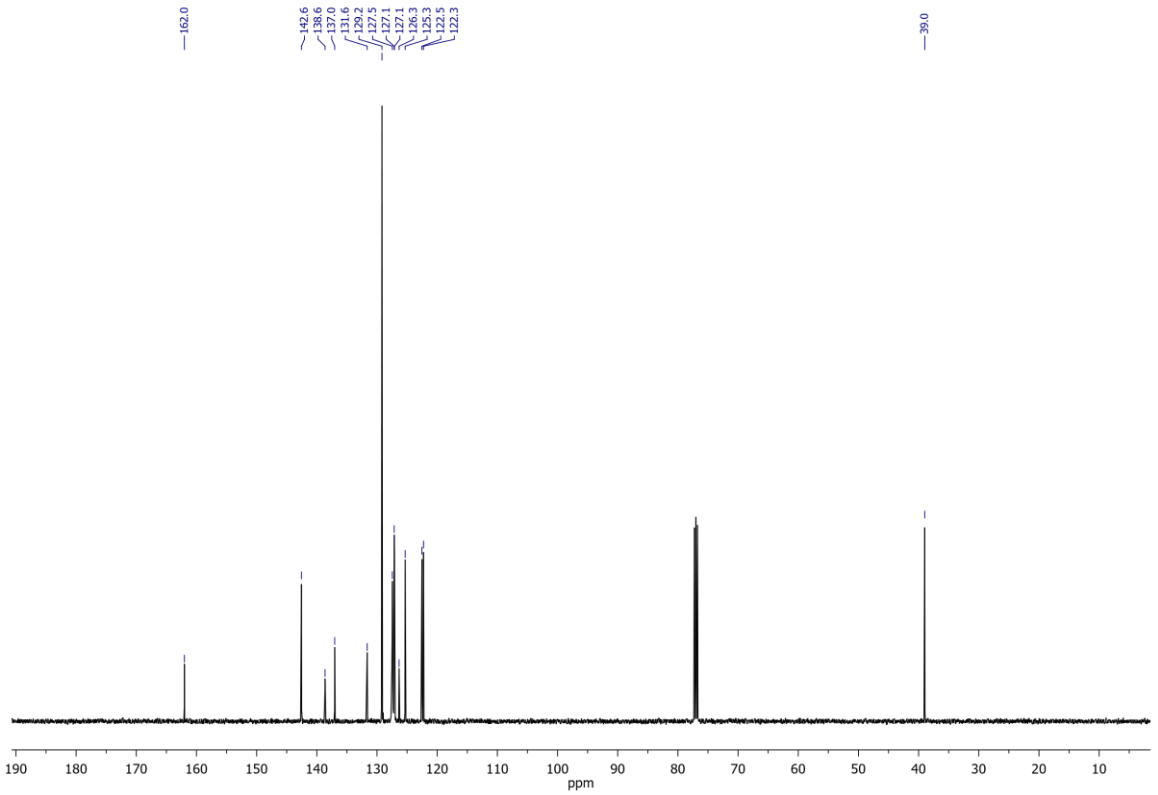


Figure S7. [13]C NMR spectrum of 2-(diphenylcarbamoyl)benzo[*b*]thiophen-3-yl methanesulfonate (**2**)

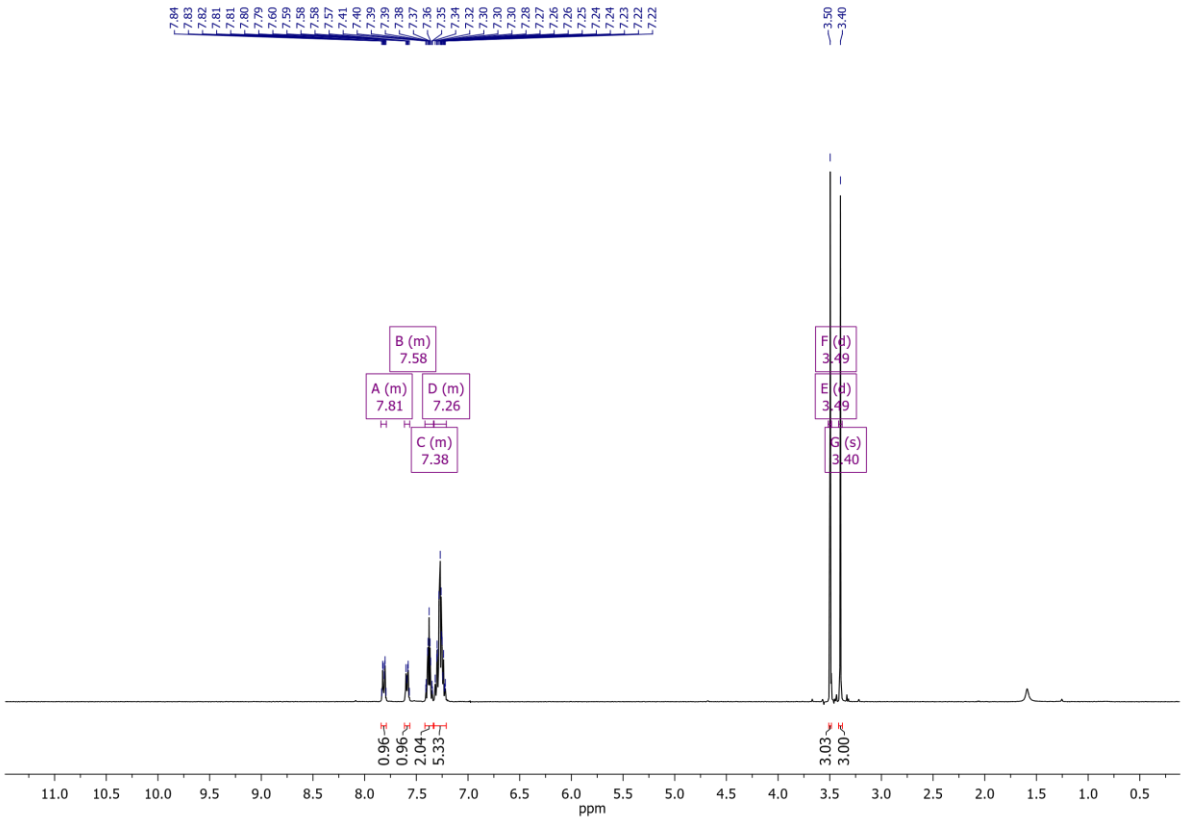


Figure S8. [1]H NMR spectrum of 2-(*N*-methyl-*N*-phenylcarbamoyl)benzo[*b*]thiophen-3-yl methanesulfonate (**3**).

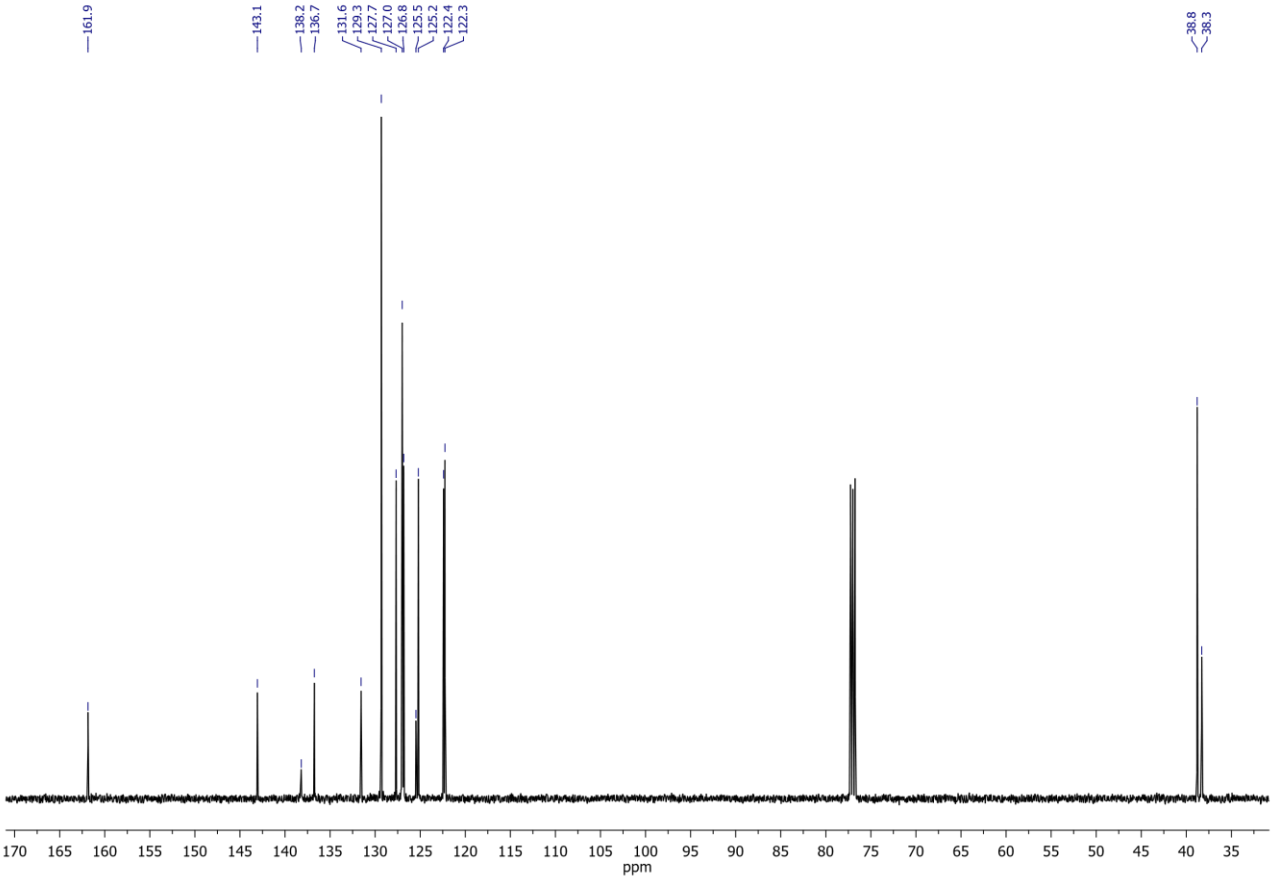


Figure S9. [13]C NMR spectrum of 2-(*N*-methyl-*N*-phenylcarbamoyl)benzo[*b*]thiophen-3-yl methanesulfonate (**3**).

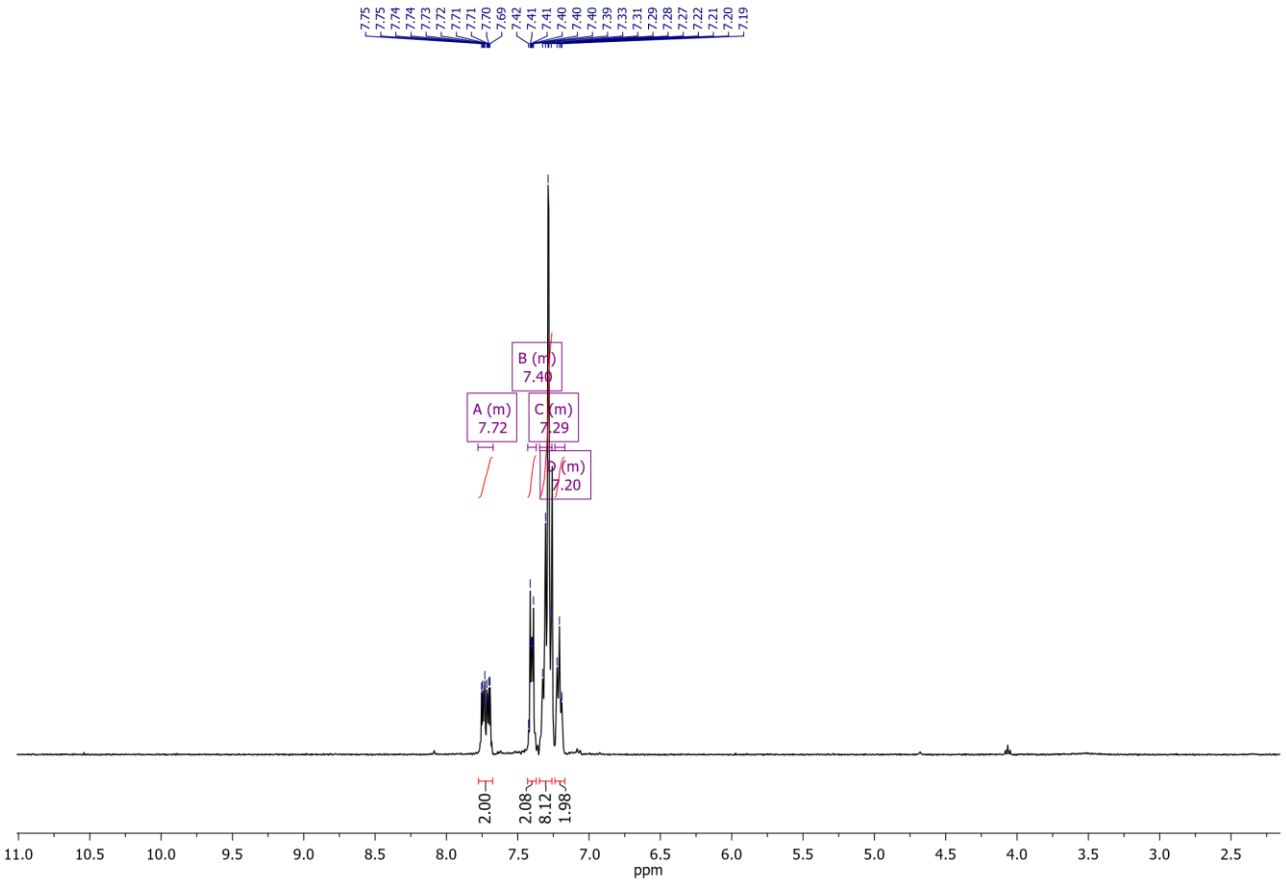


Figure S10. ^{1}H NMR spectrum of 3-chloro-*N*,*N*-diphenylbenzo[*b*]thiophene-2-carboxamide (**4**).

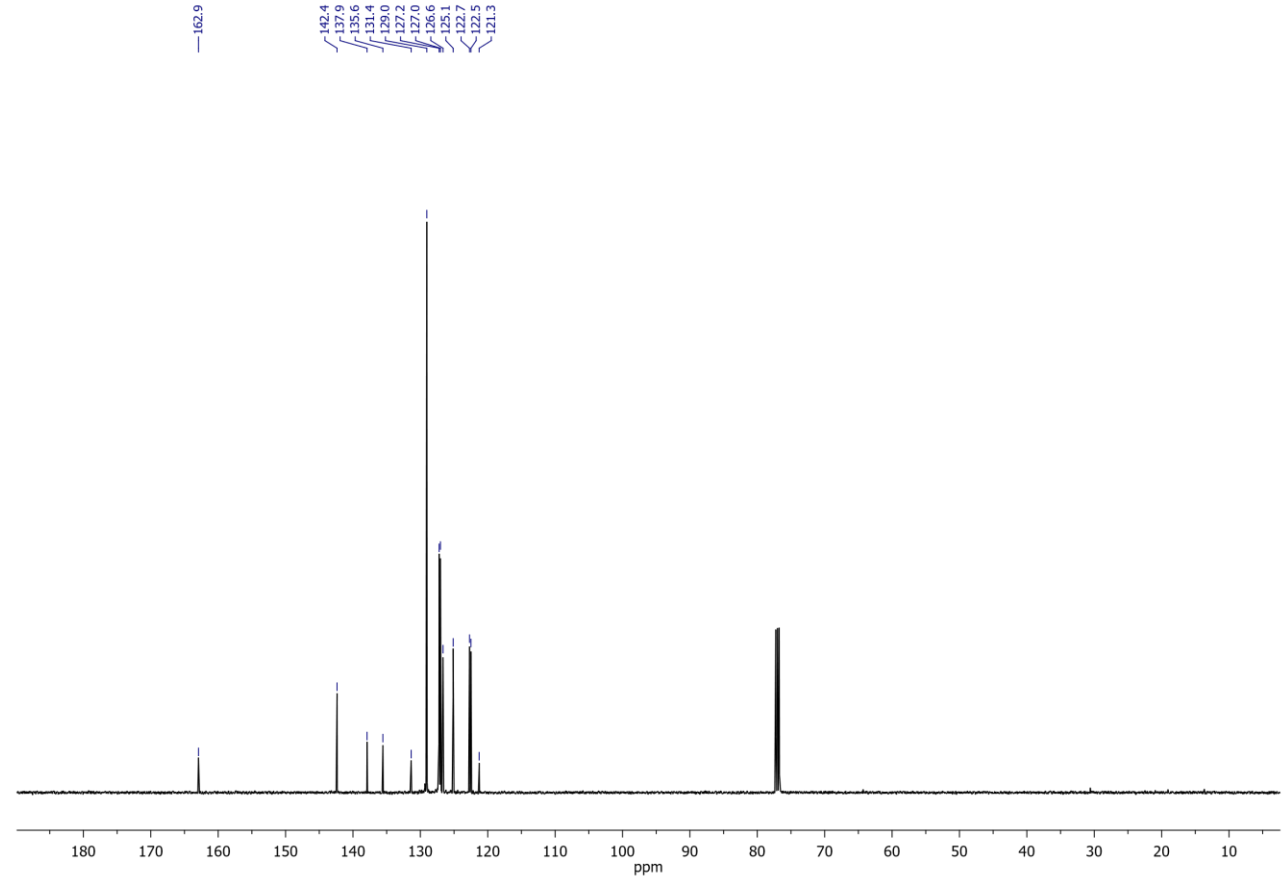


Figure S11. ^{13}C NMR spectrum of 3-chloro-*N*,*N*-diphenylbenzo[*b*]thiophene-2-carboxamide (**4**).