Electronic Supplementary Information

Microwave assisted Cobalt(III)-catalysed C-H aminocarbonylation reactions with isocyanates for the synthesis of thiophenecarboxamides

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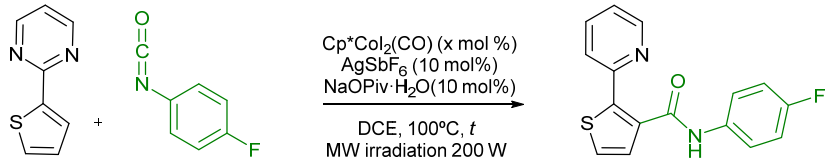
1. ADDITIONAL EXPERIMENTS

1.1. Preliminary essays at different reaction times and catalyst loading

After a brief optimisation of the catalyst loading and time (Table S1), amide **3a** could be obtained in an excellent 90% yield at 100º C in a sealed reaction tube under MW irradiation with a maximum power of 200 W after only 1 hour (Table S1, entry 6). The catalyst loading could be reduced from 5 mol% to 2.5 mol% without a big erosion of the yield (82% (Table S1, entry 4). Further reduction of the cobalt catalyst loading to 1.5 mol% resulted in a significant reduction of the yield (Table S1, entries 1-3).

Table S1. Optimization of catalyst loading, time and temperature.

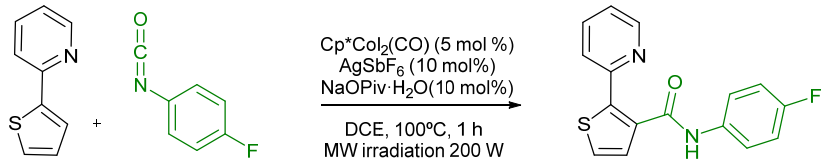


1a **2a** **3a**

Entry	% mol Cp*Co(III)	t (min)	T (ºC)	3a (%)
1	1.25	60	100	39
2	1.25	120	100	59
3	1.25	180	100	72
4	2.5	60	100	82
5	2.5	60	80	74
6	5	30	100	67
7	5	60	100	90

1.2. Aminocarbonylation reaction of 1b and 1c,d.

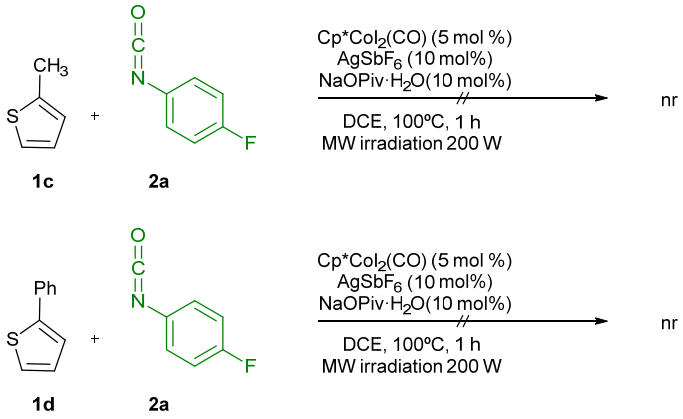
The efficiency of pyridine as directing group, instead of pyrimidine, was also tested. 2-(Thiophen-2-yl)pyridine (**1b**) was used as substrate under the optimized reaction conditions for the reaction with **2a**, obtaining a significantly lower yield of the corresponding amide **1b** (50%). Therefore, we continued the extension of the reaction using **1a** as substrate (Table 3).



1b **2a** **3ba** (50%)

Scheme S1. Aminocarbonylation reaction of **1b**.

We also checked that the presence of a directing group is necessary to control regioselectivity and enhance reactivity. Indeed, when 2-methylthiophene (**1c**) and 2-phenylthiophene (**1d**) were used as substrates, no reaction was observed with **2a** under the optimized conditions (Scheme S2)



Scheme S2. Attempts of aminocarbonylation reactions of **1c** and **1d**

2. EXPERIMENTAL SECTION

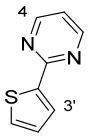
2.1. GENERAL EXPERIMENTAL METHODS

Melting points were determined in unsealed capillary tubes and are uncorrected. IR spectra were obtained using an ATR. NMR spectra were recorded at 20-25 ˚C, at 300 MHz for ^{1}H and 75.5 MHz for ^{13}C in $CDCl_3$ solutions. Assignments of individual ^{13}C and ^{1}H resonances are supported by DEPT experiments and 2D correlation experiments (COSY, HSQC or HMBC) when necessary. Mass spectra were recorded under electron impact (EI) at 70 eV, chemical ionization (CI) at 230 eV, or with an ESI^{+} source. Exact mass was obtained using a TOF detector. TLC was carried out with 0.2 mm thick silica gel plates. Visualization was accomplished by UV light. Flash column chromatography was performed on silica gel (230-400 mesh). All solvents used in reactions were anhydrous and purified according to standard procedures. All air- or moisture-sensitive reactions were performed under argon; the glassware was dried (130 ˚C) and purged with argon. Heating blocks with temperature control were used for the reactions that required heating. MW assisted reactions were carried out using a CEM Discover Lab Mate Reactor. The reaction temperature was measured by an integrated infrared sensor, and the reaction times indicated refer to the time at the given temperature. The maximum power supplied to reach the stated temperature was 200 W. Palladium catalysts were commercially available, and were used without further purification: $Pd_2(dba)_3$ (97% purity), $Pd(OAc)_2$ (98%), $Pd(PPh_3)_4$ (99%). Cp*Co(III) catalyst [$Cp^*Co(CO)I_2$] was prepared and characterized according to literature procedures.[1]

[1] B. Sun, T. Yoshino, S. Matsunaga and M. Kanai, *Adv. Synth. Catal*. 2014, **356**, 1491-1495.

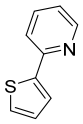
2.2. SYNTHESIS OF SUBSTRATES 1a,b, 4a,b and 6a,b

2-(Thiophen-2-yl)pyrimidine (1a).[2] Under argon atmosphere, a mixture of 2-chloropyrimidine



(229.1 mg, 2 mmol), 2-thiophene boronic acid (353.9 mg, 3 mmol), K_3PO_4 (849.1 mg, 4 mmol), $Pd_2(dba)_3$ (18.1 mg, 0.04 mmol) and XPhos (38.1 mg, 0.16 mmol) in *tert*-amyl alcohol (4 mL) was heated to 100 °C for 5 h with 3 Å molecular sieve. The mixture was passed through a short plug of silica gel with ethyl acetate, solvent was removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether/EtOAc 8/2) affording **1a** as white solid (233.3 mg, 72%), whose data were coincidental to those reported: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.62 (d, J = 4.9 Hz, 2H, H4, H6), 7.98 (dd, J = 3.7, 1.2 Hz, 1H, H3'), 7.44 (dd, J = 5.0, 1.2 Hz, 1H, H5'), 7.10 (dd, J = 5.0, 3.7 Hz, 1H, H4'), 7.00 (t, J = 4.9 Hz, 1H, H5) ppm; ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 161.5 (C2), 157.2 (C4, C6), 143.2 (C2'), 129.9, 129.0 (C3', C5'), 128.3 (C4'), 118.5 (C5) ppm.

2-(Thiophen-2-yl)pyridine (1b)[3]. Under argon atmosphere, a mixture of pyridin-2-yl 4-

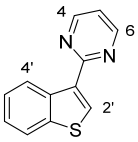


methylbenzenesulfonate (1556.7 mg, 6.2 mmol), 2-thienyl boronic acid (879.8 mg, 7.5 mmol), XPhos (71.5 mg, 0.15 mmol), $Pd(OAc)_2$ (26.4 mg, 0.12 mmol) in dry *n*-butanol was stirred for 15 min at room temperature. Then, a solution of NaOH (421.6 mg) in degassed H_2O (8.4 mL) was added and the mixture was stirred at room temperature for 45 min. The mixture was passed through a short plug of silica gel with ethyl acetate, the solvent was removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether/EtOAc 7/3) leading to **1b** as light brown solid (994.9 mg, 99 %), whose data were coincidental to those reported: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.59 (d, J = 5.4 Hz, 1H, H6). 7.65-7.75 (m, 2H, H3, H4), 7.60 (dd, J = 3.8, 1.2 Hz, 1H, H3'), 7.42 (dd, J = 5.1, 1.2 Hz, 1H, H5'), 7.10-7.25

[2] K. Billingsley and S. L. Buchwald, *J. Am. Chem. Soc.,* 2007, **129**, 3358.
[3] J. Yang, S. Liu, J-F. Zheng and J. Zhou, *Eur. J. Org. Chem.,* 2012, 6248.

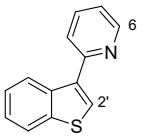
(m, 2H, H4', H5) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 152.6 (C2), 149.5 (C6), 144.8 (C2'), 136.6 (C4), 128.0 (C5'), 127.5 (C4'), 124.5 (C3'), 121.9 (C3), 118.8 (C5) ppm.

2-(Benzo[*b*]thiophen-3-yl)pyrimidine (4a).[4] Under argon atmosphere, a solution of



benzo[*b*]thien-3-ylboronic acid (225.9 mg, 1.27 mmol), 2-chloropyrimidine (127.2 mg, 1.11 mmol), $Pd(PPh_3)_4$ (0.005 mmol, 6.3 mg) and Na_2CO_3 (1.02 mmol, 216.3 mg) in DME (3 mL) and H_2O (1 mL). was heated at 110º C for 20 h. Once at room temperature, AcOEt (5 mL) was added, and the crude reaction mixture was washed with $NaHCO_3$ (10% aq., 5 mL). The aqueous phse was extracted with AcOEt (3 x 10 mL) dried over sodium sulphate, filtered, and concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc 9/1) afforded **4a** as white solid (221.6 mg, 94%), whose data are coincidental to those reported: mp: 80-82 °C (Lit:[4] 86 ºC); ^1H NMR (300 MHz, $CDCl_3$) δ 9.14 (dd, *J* = 8.0, 1.4 Hz, 1H, H4'), 8.86 (d, *J* = 4.9 Hz, 2H, H4, H6), 8.62 (s, 1H, H2'), 7.94 (dt, *J* = 8.1, 1.1 Hz, 1H, H7'), 7.53 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H, H6'), 7.49 – 7.38 (m, 1H, H5'), 7.20 (t, *J* = 4.9 Hz, 1H, H5) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 162.5 (C2), 156.9 (C4, C6), 141.1 (C7a'), 137.0 (C3a'), 134.6 (C3'), 132.1 (C6'), 125.8, 124.9, 124.6 (C5', C4', C7'), 122.6 (C2'), 118.5 (C5) ppm.

2-(Benzo[*b*]thiophen-3-yl)pyridine (4b).[5] Under argon atmosphere, benzo[*b*]thien-3-ylboronic

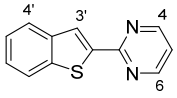


acid (640.9 mg, 3.6 mmol), *n*-butanol (4.5 mL) and 2-bromopyridine (0.29 mL, 3 mmol). The mixture was purged with argon for 30 min; then degassed sodium hydroxide aqueous solution (1.5 mL, 4 M) was slowly added. To this mixture add $Pd(OAc)_2$ (13.5 mg, 0.06 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (21.8 mg, 0.075 mmol). The resulting reaction mixture was stirred for 6 h at room temperature. Then, reaction

[4] C. Zhu, T. Pinkert, S. Greβies and F. Glorius, *ACS Catal.,* 2018, **8**, 10036.
[5] B. Qu, H. P. R. Mangunuru, S. Tcyrulnikov.; D. Rivalti, O. V. Zatolochnaya, D. Kurouski, S. Radomkit, S. Biswas, S. Karyakarte, K. R. Fandrick, J. D. Sieber, S. Rodriguez, J.-N. Desrosiers, N. Haddad, K. McKellop, S. Pennino, H. Lee, N. K. Yee, J. J. Song, M. C. Kozlowski and C. H. Senanayake, *Org. Lett*., 2018, **20**, 1333.

was stopped with addition of water (10 mL) and extracted with ethyl acetate (3 x 15 mL), dried over sodium sulphate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, petroleum ether/EtOAc 9/1) affording **5a** as colourless oil (466.4 mg, 74 %), whose data are coincidental to those reported:[3] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.78 (d, J = 4.8 Hz, 1H, H6), 8.45-8.54 (m, 1H, H4'), 7.90-7.99 (m, 1H, H7'), 7.77-7.87 (m, 2H, H4, H2'), 7.67-7.77 (m, 1H, H3), 7.37-7.53 (m, 2H, H5',H6'), 7.25-7.35 (m, 1H, H5) ppm; ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$) δ 154.7 (C2), 149.7 (C6), 140.9 (C3a'), 137.3 (C7a'), 136.7 (C4), 136.6 (C6'), 126.4 (C5'), 124.7, 124.6 (C3, C3'), 124.1 (C4'), 122.7 (C5), 122.6 (C7'), 122.0 (C2') ppm.

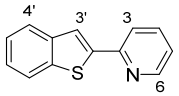
2-(Benzo[*b*]thiophen-2-yl)pyrimidine (6a). Under argon atmosphere, a solution of



benzo[*b*]thien-2-ylboronic acid (538 mg, 3.02 mmol), 2-chloropyrimidine (230 mg, 2.02 mmol), $Pd(PPh_3)_4$ (115 mg, 0.10 mmol,) and K_2CO_3 (577 mg, 4.17 mmol) in toluene (10 mL), ethanol (3 mL) and H_2O (10 mL) was heated at 110º C for 20 h. Once at room temperature, saturated aq. NH_4Cl (5 mL) was added, and the crude reaction mixture was extracted with AcOEt (3 x 10 mL). The organic phase was dried over sodium sulphate, filtered, and concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc 7/3) afforded **6a** as white solid (178.1 mg, 42%), whose data are coincidental to those reported:[6] ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.14 (ddd, J = 8.1, 1.4, 0.7 Hz, 1H, H7'), 8.85 (d, J = 4.9 Hz, 2H, H4, H6), 8.62 (s, 1H, H3'), 7.94 (ddd, J = 8.1, 1.4, 0.7 Hz, 1H, H4'), 7.53 (td, J = 8.1, 1.4 Hz, 1H, H6'), 7.47 – 7.40 (m, 1H, H5'), 7.20 (t, J = 4.9 Hz, 1H, H5) ppm; ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$) δ 162.6 (C2), 157.0 (C4, C6), 141.0 (C2'), 137.0 (C3a'), 134.6 (C7a'), 132.0 (C6'), 125.6 , 124.8, 124.6 (C5', C4', C7'), 122.6 (C3'), 118.5 (C5) ppm.

[6] D.-D. Lu, X.-X. He and F. S. Liu, *J. Org. Chem.*, 2017, **82**, 10898.

2-(Benzo[*b*]thiophen-2-yl)pyridine (6b).[7] Under argon atmosphere, a solution of benzo[*b*]thien-



2-ylboronic acid (536.8 mg, 3.02 mmol), 2-bromopyridine (0.19 mL, 2.00 mmol), $Pd(PPh_3)_4$ (115.2 mg, 0.10 mmol,) and K_2CO_3 (573.6 mg, 4.16 mmol) in toluene (10 mL), ethanol (3 mL) and H_2O (10 mL) was heated at 110º C for 20 h. Once at room temperature, saturated aq. NH_4Cl (5 mL) was added, and the crude reaction mixture was extracted with AcOEt (3 x 10 mL). The organic phase was dried over sodium sulphate, filtered, and concentrated under reduced pressure. Purification by column chromatography (silica gel, petroleum ether/EtOAc 7/3) afforded **6b** as white solid (178.1 mg, 42%), whose data are coincidental to those reported: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.66 (ddd, J = 4.9, 1.8, 1.2 Hz, 1H, H6), 7.92 – 7.73 (m, 5H, H3', H4', H7', H3, H4), 7.42 – 7.35 (m, 2H, H5', H6'), 7.24 (ddd, J = 7.3, 4.9, 1.2 Hz, 1H, H5) ppm; ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$) δ 152.5 (C2), 149.7 (C6), 144.8 (C2'), 140.6 (C3a'), 140.4 (C7a'), 136.6 (C4), 128.5 (C6'), 125.0 (C5'), 124.5, 124.1 (C3, C5), 122.6 (C4'), 121.1 (C7'), 119.5 (C3') ppm.

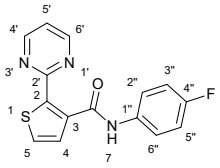
2.3. AMINOCARBONYLATION REACTION. GENERAL PROCEDURE. SYNTHESIS OF AMIDES 3, 5 AND 7

Under argon atmosphere, a sealable reaction tube (10 mL, 1.3 × 9 cm) equipped with a stirring bar was charged with corresponding (benzo)tiophene **1, 4** or **6** (0.5 mmol), $NaOPiv{\cdot}H_2O$ (0.05 mmol), $Cp^*Co(CO)I_2$ (0.0125 or 0.025 mmol), $AgSbF_6$ (0.05 mmol) and the corresponding isocyanate **2** (1 mmol). DCE was added (2 mL), and the mixture was stirred for 2 min until solids were dissolved. Then, the reaction tube was sealed and heated under microwave irradiation at 100 °C for 1 h, using a maximum power of 200 W. After cooling to room temperature, the mixture was filtered through silica gel and eluted with ethyl acetate. Then, the solvent was

[7] J. Pospech, A. Tlili, A. Spannenberg, H. Neumann and M. Beller, *Chem. Eur. J.*, 2014, **20**, 3135.

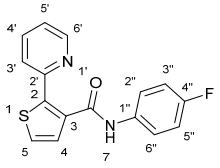
evaporated under vacuum and the residue was purified by column chromatography affording corresponding amides **3**, **5** or **7**.

***N*-(4-Fluorophenyl)-2-(pyrimidin-2-yl)thiophene-3-carboxamide (3a).** According to the General



Procedure, **1a** (0.49 mmol, 81.0 mg) was treated with 4-fluorophenyl isocyanate **2a** (1.0 mmol, 0.11 mL), Cp*Co(CO)I_2 (0.025 mmol, 11.8 mg), $AgSbF_6$ (0.05 mmol, 17.5 mg), NaOPiv·H_2O (0.054 mmol, 7.8 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 70:30:1), **3a** was obtained as a white solid (133.9 mg, 90%): mp (CH_2Cl_2): 172-174 ºC; IR (ATR): 3285, 1630 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.87 (d, J = 4.9 Hz, 2H, H4', H6'), 7.99 (d, J = 5.3 Hz, 1H, H5), 7.75 (dd, J = 9.0 Hz, 4.8 Hz, 2H, H2'', H6''), 7.50 (d, J = 5.3 Hz, 1H, H4), 7.33 (t, J = 4.9 Hz, 1H, H5'), 7.09 (t, J = 9 Hz, 2H, H3'', H5'') ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 160.8 (C=O), 160.5 (C2'), 159.2 (d, J = 243.1 Hz, C4''), 156.6 (C4', C6'), 140.5 (C2), 138.2 (C3), 135.1 (d, J = 2.6 Hz, C1''), 134.9 (C4), 128.6 (C5), 121.8 (d, J = 7.8 Hz, C2'', C6''), 119.2 (C5'), 115.6 (d, J = 22.3 Hz, C3'', C5'') ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ -118.50 ppm; MS (ESI): *m/z* (rel intensity): 300 (MH^+, 37), 249 (2), 189 (100); HRMS (ESI-TOF): calcd. for $C_{15}H_{11}FN_3OS$ [MH^+]: 300.0601; found: 300.0611.

***N*-(4-Fluorophenyl)-2-(pyridin-2-yl)thiophene-3-carboxamide (3ba).** According to the General



Procedure, **1b** (0.41 mmol, 66.0 mg) was treated with 4-fluorophenyl isocyanate **2a** (0.8 mmol, 0.11 mL), Cp*Co(CO)I_2 (0.02 mmol, 9.6 mg), $AgSbF_6$ (0.05 mmol, 19.1 mg), NaOPiv·H_2O (0.056 mmol, 7.9 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 70:30:1), **3ba** was obtained as a white solid (61.6 mg, 50%): mp (CH_2Cl_2): 176-178 ºC; IR (ATR): 3290, 1655 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.77 – 8.69 (m, 1H, H6'), 7.91 – 7.68 (m, 5H, H4, H5, H3', H4', H5'), 7.44 – 7.34 (m, 2H, H2'', H6''), 7.06 (t, J = 8.8 Hz, 2H, H3'', H5'') ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 161.2 (C=O), 158.5 (J = 240.7 Hz, C4''), 152.1 (C2), 147.4 (C6'), 140.49

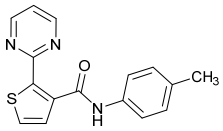
(C2'), 138.2 (C4'), 136.6 (C3), 135.1 (*J* = 3.0 Hz, C1''), 133.6 (C4), 125.16(C3'), 124.9 (C5'), 123.2 (C5), 121.5 (*J* = 7.5 Hz, C2'', C6''), 115.5 (*J* = 21.7 Hz, C3'', C5'') ppm; ^{19}F NMR (282 MHz, $CDCl_3$) *δ* -118.73 ppm; HRMS (ESI-TOF): calcd for $C_{16}H_{12}FN_2OS$ [MH^+]: 299.0649; found: 299.0648.

***N*-Phenyl-2-(pyrimidin-2'-yl)thiophene-3-carboxamide (3b).** According to the General Procedure, **1a** (0.49 mmol, 80.7 mg) was treated with phenylisocyanate **2b** (1.0 mmol, 0.11 mL), Cp*Co(CO)I_2 (0.023 mmol, 11.1 mg), $AgSbF_6$ (0.05 mmol, 19.1 mg), NaOPiv·H_2O (0.051 mmol, 7.3 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 80:20:1), **3b** was obtained as a yellow solid (61.6 mg, 50%): mp (CH_2Cl_2): 160-163 ºC; IR (ATR): 3080, 1629 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 8.86 (d, *J* = 4.9 Hz, 2H, H4', H6'), 7.99 (d, *J* = 5.4 Hz, 1H, H4), 7.84 – 7.75 (m, 2H, H5, H5'), 7.48 – 7.28 (m, 4H, H, H2'', H3'', H5'', H6''), 7.05-7.18 (m, 1H, H4'') ppm; ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$) *δ* 160.9 (C=O), 160.6 (C2'), 156.6 (C4', C6'), 140.4 (C2), 139.0 (C3), 138.4 (C1''), 134.9 (C4), 129.0 (C3'', C5''), 128.5 (C4''), 124.0 (C2'', C6''), 120.3 (C5), 119.1 (C5') ppm; MS (ESI): *m/z* (rel intensity): 282 (MH^+, 25), 190 (8), 189 (100); HRMS (ESI-TOF): calcd for $C_{15}H_{12}N_3OS$ [MH^+]: 282.0696; found: 282.0703.

***N*-(4-Chlorophenyl)-2-(pyrimidin-2-yl)thiophene-3-carboxamide (3c).** According to the General Procedure, **1a** (0.5 mmol, 80.7 mg) was treated with 4-chlorophenylisocyanate **2c** (1.0 mmol, 157.1 mg), Cp*Co(CO)I_2 (0.012 mmol, 5.61 mg), $AgSbF_6$ (0.05 mmol, 19.1 mg), NaOPiv·H_2O (0.05 mmol, 6.5 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 70:30:1), **3c** was obtained as a yellow solid (110.5 mg, 69%): mp (CH_2Cl_2): 214-218 ºC; IR (ATR): 3002, 1622 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 8.78 (d, *J* = 5.0 Hz, 2H, H4', H6'), 7.89 (d, *J* = 5.4 Hz, 1H, H5), 7.66 (*J* = 9.0 Hz, 2H, H2'', H6''), 7.40 (d, *J* = 5.4 Hz, 1H, H4), 7.31 – 7.21 (m, 3H, H5', H3'', H5'') ppm; ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$) *δ* 160.8 (C2'), 160.5 (C=O), 156.6 (C4', C6'), 138.5 (C2), 138.1 (C3), 137.6 (C1''), 134.9 (C4), 129.0 (C3'', C5''), 128.7 (C4''), 128.6 (C5), 121.4 (C2'', C6''), 119.1

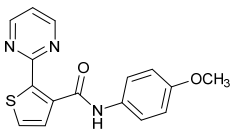
(C5') ppm; MS (ESI): *m/z* (rel intensity): 318 (MH^++2, 8), 316 (MH^+, 26), 191 (3), 190 (7), 189 (100); HRMS (ESI-TOF): calcd for $C_{15}H_{11}ClN_3OS$ [MH^+]: 316.0306; found: 316.0311.

2-(Pyrimidin-2-yl)-*N*-(p-tolyl)thiophene-3-carboxamide (3d). According to the General



Procedure, **1a** (0.52 mmol, 85.1 mg) was treated with *p*-tolylisocyanate **2c** (1.0 mmol, 0.12 mL), $Cp^*Co(CO)I_2$ (0.027 mmol, 13 mg), $AgSbF_6$ (0.06 mmol, 21.1 mg), $NaOPiv{\cdot}H_2O$ (0.05 mmol, 6.5 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 70:30:1), **3d** was obtained as a white solid (82.6 mg, 53%): mp (CH_2Cl_2): 165-167 ºC; IR (ATR): 3070, 1665 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 13.35 (s, 1H, NH), 8.77 (d, *J* = 4.9 Hz, 2H, H4', H6'), 7.94 (d, *J* = 5.4 Hz, 1H, H5), 7.74 – 7.54 (m, 2H, H2'', H6''), 7.43 (d, *J* = 5.4 Hz, 1H, H4), 7.24 (t, *J* = 4.9 Hz, 1H, H5'), 7.16 (d, *J* = 8.2 Hz, 2H, H3'', H5''), 2.34 (s, 3H, CH_3) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 160.7, 160.4 (C=O, C2'), 156.6 (C4', C6'), 140.4 (C2), 138.5 (C3), 136.5 (C1''), 134.9 (C4), 133.5 (C4''), 129.5 (C3'', C5''), 128.4 (C5), 120.2 (C2'', C6''), 119.1 (C5'), 21.0 (CH_3) ppm; MS (ESI): *m/z* (rel intensity): 296.0858 (MH^+, 36), 191 (3), 189 (100); HRMS (ESI-TOF): calcd for $C_{16}H_{14}N_3OS$ [MH^+]: 296.0852; found: 296.0855.

***N*-(4-Methoxyphenyl)-2-(pyrimidin-2-yl)thiophene-3-carboxamide (3e).** According to the



General Procedure, **1a** (0.49 mmol, 80.5 mg) was treated with 4-methoxyphenyl isocyanate **2e** (1.01 mmol, 0.13 mL), $Cp^*Co(CO)I_2$ (0.025 mmol, 11.8 mg), $AgSbF_6$ (0.068 mmol, 23.5 mg), $NaOPiv{\cdot}H_2O$ (0.05 mmol, 6.5 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 60:40:1), **3e** was obtained as a white solid (46 mg, 29%): mp (CH_2Cl_2): 176-178 ºC; IR (ATR): 3083, 1658 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 13.30 (s, 1H, NH), 8.80 (d, *J* = 4.9 Hz, 2H, H4', H6'), 7.95 (d, *J* = 5.4 Hz, 1H, H5), 7.72 – 7.63 (m, 2H, H2'', H6''), 7.45 (d, *J* = 5.4 Hz, 1H, H4), 7.26 (t, *J* = 4.9 Hz, 1H, H5'), 6.95 – 6.86 (m, 2H, H3'', H5''), 3.82 (s, 3H, OCH_3) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 160.8, 160.3 (C=O, C2'), 156.6 (C4', C6'), 156.1 (C4''), 140.2 (C2), 138.6 (C3), 134.9 (C4),

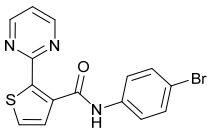
132.3(C1''), 128.5 (C5), 121.7 (C2'', C6''), 119.1 (C5'), 114.2 (C3'', C5''), 55.5 (OCH_3) ppm; MS (ESI): *m/z* (rel intensity): 312 (MH^+, 44), 191 (3), 190 (8), 189 (100); HRMS (ESI-TOF): calcd for $C_{16}H_{14}N_3O_2S$ [MH^+]: 312.0801; found: 312.0804.

***N*-(4-Acetylphenyl)-2-(pyrimidin-2-yl)thiophene-3-carboxamide (3f).** According to the General Procedure, **1a** (0.5 mmol, 81.1 mg) was treated with 4-acetylphenyl isocyanate **2f** (1.04 mmol, 168 mg), Cp*Co(CO)I_2 (0.025 mmol, 11.8 mg), $AgSbF_6$ (0.054 mmol, 20.4 mg), NaOPiv·H_2O (0.05 mmol, 6.5 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 60:40:1), **3f** was obtained as a white solid (57.4 mg, 35%): mp (CH_2Cl_2): 172-175 ºC; IR (ATR): 3093, 1669 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 13.84 (s, 1H, NH), 8.84 (d, *J* = 4.9 Hz, 2H, H4', H6'), 7.90 – 8.01 (m, 3H, H2'', H6'', H5), 7.83 (d, *J* = 8.8 Hz, 2H, H3'', H5''), 7.46 (d, *J* = 5.4 Hz, 1H, H4), 7.32 (t, *J* = 4.9 Hz, 1H, H5'), 2.58 (s, 3H, CH_3) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 197.0 ($\underline{C}OCH_3$), 160.8, 160.6 (C=O, C2'), 156.6 (C4', C6'), 143.5(C2), 141.0 (C1''), 137.8 (C3), 134.9 (C4), 132.5 (C4''), 129.8 (C2'', C6''), 128.8(C5), 119.4 (C5'), 119.3(C3'', C5''), 26.4 ($CO\underline{C}H_3$) ppm; MS (ESI): *m/z* (rel intensity): 324 (MH^+, 38), 191 (3), 190 (7), 189 (100); HRMS (ESI-TOF): calcd for $C_{17}H_{14}N_3O_2S$ [MH^+]: 324.0801; found: 324.0807.

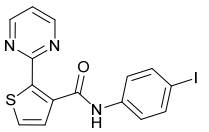
***N*-(3-Chloro-4-methylphenyl)-2-(pyrimidin-2-yl)thiophene-3-carboxamide (3g).** According to the General Procedure, **1a** (0.51 mmol, 82.4 mg) was treated with 3-chloro-4-methylphenyl isocyanate **2g** (1.02 mmol, 0.14 mL), Cp*Co(CO)I_2 (0.012 mmol, 5.7 mg), $AgSbF_6$ (0.05 mmol, 17.3 mg), NaOPiv·H_2O (0.051 mmol, 7.3 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 60:40:1), **3g** was obtained as a white solid (68 mg, 40%): mp (CH_2Cl_2): 193-196 ºC; IR (ATR): 3070, 1665 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 13.54 (s, 1H, NH), 8.84 (d, *J* = 4.9 Hz, 2H, H4', H6'), 7.95 (d, *J* = 5.4 Hz, 1H, H5), 7.84 (d, *J* = 2.2 Hz, 1H, H2''), 7.53 (dd, *J* = 8.2, 2.2 Hz, 1H, H6''), 7.47 (d, *J* = 5.4 Hz, 1H, H4), 7.27 – 7.36 (m, 1H, H5'), 7.20 (d, *J* = 8.2 Hz, 1H, H5''), 2.36 (s, 3H, CH_3) ppm;

$^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$) δ 160.8, 160.5 (C=O, C2'), 156.6 (C4', C6'), 140.5 (C2), 138.2 (C1''), 137.9 (C3), 135.0 (C3''), 134.5 (C4), 131.3 (C4''), 131.0 (C5''), 128.6 (C5), 120.7(C2''), 119.2(C6''), 118.4 (C5'), 19.5 (CH_3) ppm; MS (ESI): *m/z* (rel intensity): 332 (MH^++2, 11), 330 (MH^+, 33), 191 (3), 190 (7), 189 (100); HRMS (ESI-TOF): calcd for $C_{16}H_{13}ClN_3OS$ [MH^+]: 330.0462; found: 330.0471.

***N*-(4-Bromophenyl)-2-(pyrimidin-2-yl)thiophene-3-carboxamide (3h).** According to the General Procedure, **1a** (0.51 mmol, 83.7 mg) was treated with 4-bromophenyl isocyanate **2h** (1.03 mmol, 204.6 mg), Cp*Co(CO)I_2 (0.015 mmol, 7.2 mg), $AgSbF_6$ (0.051 mmol, 17.7 mg), NaOPiv·H_2O (0.06 mmol, 8.5 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt 60:40), **3h** was obtained as a brownish solid (122 mg, 66%): mp (CH_2Cl_2): 209-212 ºC; IR (ATR): 3292, 1623 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ): 8.88 (d, *J* = 4.9 Hz, 2H, H4', H6'), 7.98 (d, *J* = 5.4 Hz, 1H, H4), 7.71 (d, *J* = 8.7 Hz, 2H, H2'', H6''), 7.56 – 7.46 (m, 3H, H5, H3'', H5''), 7.35 (t, *J* = 4.9 Hz, 1H, H5') ppm; $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$) δ 160.8, 160.5 (C=O, C2'), 156.6 (C4', C6'), 140.5 (C2), 138.1 (C1''), 134.9 (C3), 131.9 (C4, C3'', C5''), 128.7 (C4''), 121.7 (C2'', C6''), 119.1 (C5), 116.4 (C5') ppm; MS (ESI): *m/z* (rel intensity): 361 (MH^++2, 25), 359 (MH^+, 24), 191 (2), 190 (6), 189 (100); HRMS (ESI-TOF): calcd for $C_{15}H_{11}BrN_3OS$ [MH^+]: 359.9801; found: 359.9809.

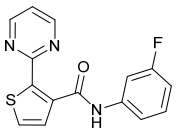


***N*-(4-Iodophenyl)-2-(pyrimidin-2-yl)thiophene-3-carboxamide (3i).** According to the General Procedure, **1a** (0.504 mmol, 81.9 mg) was treated with 4-iodophenyl isocyanate **2i** (1.03 mmol, 251.3 mg), Cp*Co(CO)I_2 (0.012 mmol, 5.8 mg), $AgSbF_6$ (0.052 mmol, 18.1 mg), NaOPiv·H_2O (0.054 mmol, 7.8 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 80:20:1), **3i** was obtained as a yellow solid (151.6 mg mg, 74%): mp (CH_2Cl_2): 192-194 ºC; IR (ATR): 3095, 1670 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.87 (d, *J* = 4.9 Hz, 2H, H4', H6'), 7.97 (d, *J* = 5.4 Hz, 1H, H4), 7.75 – 7.64 (m, 2H, H2'', H6''), 7.64 – 7.54 (m, 2H, H3'', H5''), 7.49 (d, *J* = 5.4 Hz, 1H, H5),



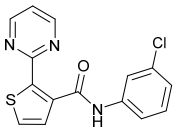
7.34 (t, *J* = 4.9 Hz, 1H, H5') ppm; $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$) δ 160.8, 160.6 (C=O, C2'), 156.6 (C4', C6'), 140.5 (C2), 138.8 (C3), 138.1 (C1''), 137.9 (C3'', C5''), 135.0 (C4), 128.7 (C5), 122.1 (C2'', C6''), 119.1 (C5'), 86.9 (C4'') ppm; MS (ESI): *m/z* (rel intensity): 407 (MH^+, 71), 313 (4), 301 (3), 191 (3), 190 (7), 189 (100); HRMS (ESI-TOF): calcd for $C_{15}H_{11}IN_3OS$ [MH^+]: 407.9662; found: 407.9670.

***N*-(3-Fluorophenyl)-2-(pyrimidin-2-yl)thiophene-3-carboxamide (3j).** According to the General



Procedure, **1a** (0.5 mmol, 83.7 mg) was treated with 3-fluorophenyl isocyanate **2j** (1.2 mmol, 0.11 mL), Cp*Co(CO)I_2 (0.012 mmol, 6.4 mg), $AgSbF_6$ (0.07 mmol, 26.5 mg), NaOPiv·H_2O (0.06 mmol, 7.5 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 70:30:1), **3j** was obtained as a white solid (123 mg, 79%): mp (CH_2Cl_2): 163-165 ºC; IR (ATR): 3065, 1677 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.74 (d, *J* = 4.9 Hz, 2H, H4', H6'), 7.85 (d, *J* = 5.4 Hz, 1H, H4), 7.62 (dt, *J* = 11.2, 2.3 Hz, 1H, H6''), 7.37 (d, *J* = 5.4 Hz, 1H, H5), 7.30 (ddd, *J* = 8.2, 2.3, 1.1 Hz, 1H, H2''), 7.25 – 7.12 (m, 2H, H5'', H5'), 6.73 (tdd, *J* = 8.2, 2.3, 1.1 Hz, 1H, H4'') ppm; $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$) δ 163.1 (*J* = 245.2 Hz, C3''), 160.7, 160.6 (C=O, C2'), 156.6 (C4', C6'), 140.7 (C2), 140.6 (*J* = 10.5 Hz, C1''), 138.0 (C3), 134.9 (C4), 130.0 (*J* = 9.7 Hz, C5''), 128.6 (C5), 119.2 (C5'), 115.4 (*J* = 3.7 Hz, C6''), 110.6 (*J* = 21.7 Hz, C2''), 107.6 (*J* = 25.5 Hz, C4'') ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ -111.5 ppm; MS (ESI): *m/z* (rel intensity): 300 (MH^+, 25), 191 (2), 190 (7), 189 (100); HRMS (ESI-TOF): calcd for $C_{15}H_{11}FN_3OS$ [MH^+]: 300.0601; found: 300.0606.

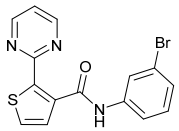
***N*-(3-Chlorophenyl)-2-(pyrimidin-2-yl)thiophene-3-carboxamide (3k).** According to the General



Procedure, **1a** (0.5 mmol, 81.2 mg) was treated with 3-chlorophenyl isocyanate **2k** (1.0 mmol, 0.13 mL), Cp*Co(CO)I_2 (0.012 mmol, 5.9 mg), $AgSbF_6$ (0.05 mmol, 17.5 mg), NaOPiv·H_2O (0.05 mmol, 6.9 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 80:20:1), **3k** was obtained as a white solid (134.7 mg, 85%): mp (CH_2Cl_2): 185-187 ºC; IR (ATR): 3008, 1675 cm^{-1}; ^{1}H NMR (300 MHz,

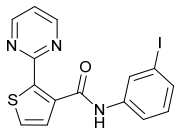
$CDCl_3$) δ 11.62 (s, 1H, NH), 8.88 (d, *J* = 4.9 Hz, 2H, H4', H6'), 7.98 (d, *J* = 5.4 Hz, 1H, H4), 7.89 (t, *J* = 2.1 Hz, 1H, H2''), 7.65 (ddd, *J* = 8.0, 2.1, 1.0 Hz, 1H, H6''), 7.49 (d, *J* = 5.4 Hz, 1H, H5), 7.38-7.29 (m, 2H, H5'', H5'), 7.12 (ddd, *J* = 8.0, 2.1, 1.0 Hz, 1H, H4'') ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 160.8, 160.6 (C=O, C2'), 156.6 (C4', C6'), 140.6 (C2), 140.2 (C1''), 138.0 (C3), 135.0 (C3''), 134.6 (C4), 129.9 (C5''), 128.7 (C5), 123.9 (C4''), 120.3 (C2''), 119.2 (C5'), 118.2 (C6'') ppm; MS (ESI): *m/z* (rel intensity): 318 (MH^++2, 6), 316 (MH^+, 19), 191 (2), 190 (7), 189 (100); HRMS (ESI-TOF): calcd for $C_{15}H_{11}ClN_3OS$ [MH^+]: 316.0306; found: 316.0310.

***N*-(3-Bromophenyl)-2-(pyrimidin-2-yl)thiophene-3-carboxamide (3l).** According to the General



Procedure, **1a** (0.5 mmol, 81.2 mg) was treated with 3-bromophenyl isocyanate **2l** (1.0 mmol, 0.13 mL), Cp*Co(CO)I_2 (0.012 mmol, 5.9 mg), $AgSbF_6$ (0.05 mmol, 17.5 mg), NaOPiv·H_2O (0.05 mmol, 6.9 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 70:30:1), **3l** was obtained as a white solid (136.7 mg, 75%): mp (CH_2Cl_2): 189-192 ºC; IR (ATR): 3098, 16738 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.88 (d, *J* = 5.0 Hz, 2H, H4', H6'), 8.09 – 7.94 (m, 1H, H2''), 7.97 (d, *J*=5.4 Hz, H4), 7.77 – 7.63 (m, 1H, H6''), 7.49 (d, *J* = 5.4 Hz, 1H, H5), 7.35 (t, *J* = 5.0 Hz, 1H, H5'), 7.28 – 7.20 (m, 2H, H4'', H5'') ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 160.8, 160.6 (C=O, C2'), 156.6 (C4', C6'), 140.6, 140.4 (C2, C3), 138.0 (C1''), 135.0 (C4), 130.2, 128.7 (C5'', C4''), 126.8 (C3''), 123.1 (C5), 122.7 (C2''), 119.2 (C6''), 118.6 (C5') ppm; MS (ESI): *m/z* (rel intensity): 361 (MH^++2, 22), 359 (MH^+, 20), 191 (2), 189 (100) ; HRMS (ESI-TOF): calcd for $C_{15}H_{11}BrN_3OS$ [MH^+]: 359.9801; found: 359.9805.

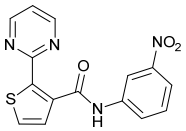
***N*-(3-Iodophenyl)-2-(pyrimidin-2-yl)thiophene-3-carboxamide (3m).** According to the General



Procedure, **1a** (0.5 mmol, 81.2 mg) was treated with 3-iodophenyl isocyanate **2m** (1.0 mmol, 0.13 mL), Cp*Co(CO)I_2 (0.012 mmol, 5.9 mg), $AgSbF_6$ (0.05 mmol, 17.5 mg), NaOPiv·H_2O (0.05 mmol, 6.9 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 80:20:1), **3m** was obtained as a white

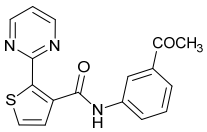
solid (143.1 mg, 70%): mp (CH_2Cl_2): 1696-171 ºC; IR (ATR): 3073, 1661 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.87 (d, *J* = 5.0 Hz, 2H, H4', H6'), 8.21 (t, *J* = 2.0 Hz, 1H, H2''), 7.97 (d, *J* = 5.4 Hz, 1H, H4), 7.75 (ddd, *J* = 8.2, 2.0, 1.0 Hz, 1H, H4''), 7.53 – 7.42 (m, 2H, H5, H6''), 7.35 (t, *J* = 5.0 Hz, 1H, H5'), 7.11 (t, *J* = 8.2 Hz, 1H, H5'') ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 160.8, 160.5 (C=O, C2'), 156.6 (C4', C6'), 140.6 (C2), 140.3 (C3), 138.0 (C1''), 135.0 (C4''), 132.8 (C4), 130.4 (C5''), 129.0 (C2''), 128.7 (C5), 119.3 (C6''), 119.2 (C5'), 94.3 (C3'') ppm; MS (ESI): *m/z* (rel intensity): 429 (MNa^+, 64), 407 (MH^+, 2), 313 (2), 191 (3), 190 (7), 189 (100); HRMS (ESI-TOF): calcd for $C_{15}H_{11}IN_3OS$ [MH^+]: 407.9662; found: 407.9664.

***N*-(3-Nitrophenyl)-2-(pyrimidin-2-yl)thiophene-3-carboxamide (3n).** According to the General



Procedure, **1a** (0.5 mmol, 81.9 mg) was treated with 3-nitrophenyl isocyanate **2n** (1.03 mmol, 169.1 mg), Cp*Co(CO)I_2 (0.025 mmol, 11.8 mg), $AgSbF_6$ (0.053 mmol, 18.3 mg), NaOPiv·H_2O (0.055 mmol, 7.9 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 60:40:1), **3n** was obtained as a white solid (126.1 mg, 77%): mp (CH_2Cl_2): 210-212 ºC; IR (ATR): 3087, 1668 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.94 (d, *J* = 5.0 Hz, 2H, H4', H6'), 8.53 (t, *J* = 2.1 Hz, 1H, H2''), 8.33 (d, *J* = 8.2 Hz, 1H, H4''), 8.05 – 7.96 (m, 2H, H5, H6''), 7.63 – 7.49 (m, 2H, H4, H5''), 7.40 (t, *J* = 5.0 Hz, 1H, H5') ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 160.8, 160.7 (C=O, C2'), 156.7 (C4', C6'), 148.6 (C3''), 141.0 (C2), 140.3 (C3), 137.6 (C1''), 135.0 (C5''), 129.9, 128.9 (C4, C5), 125.9 (C4''), 119.4 (C6''), 118.3 (C5'), 114.7 (C2'') ppm; MS (ESI): *m/z* (rel intensity): 327 (MH^+, 36), 190 (7), 189 (100); HRMS (ESI-TOF): calcd for $C_{15}H_{11}N_4O_3S$ [MH^+]: 327.0546; found: 327.0550.

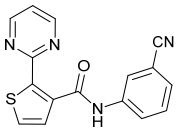
***N*-(3-Acetylphenyl)-2-(pyrimidin-2-yl)thiophene-3-carboxamide (3o).** According to the General



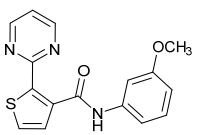
Procedure, **1a** (0.5 mmol, 82.3 mg) was treated with 3-acetylphenyl isocyanate **2o** (1.1 mmol, 187.2 mg), Cp*Co(CO)I_2 (0.025 mmol, 12.0 mg), $AgSbF_6$ (0.05 mmol, 18.3 mg), NaOPiv·H_2O (0.05 mmol, 6.9 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 60:40:1), **3o** was

obtained as a white solid (110 mg, 67%): mp (CH_2Cl_2): 172-175 ºC; IR (ATR): 3080, 1670 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.9 Hz, 2H, H4', H6'), 8.20 (t, *J* = 1.9 Hz, 1H, H2''), 8.06 (ddd, *J* = 8.1, 1.9, 1.1 Hz, 1H, H6''), 7.89 (d, *J* = 5.4 Hz, 1H, H4), 7.63 (ddd, *J* = 7.8, 1.9, 1.1 Hz, 1H, H4''), 7.45 – 7.34 (m, 2H, H5, H5''), 7.25 (t, *J* = 4.9 Hz, 1H, H5'), 2.57 (s, 3H, CH_3) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 198.0 ($\underline{C}OCH_3$), 160.7, 160.7 (C=O, C2'), 156.7 (C4', C6'), 140.7 (C2), 139.6 (C3), 138.0 (C1''), 137.7 (C3''), 134.9 (C5''), 129.3 (C4), 128.6 (C6''), 124.7 (C4''), 123.7 (C5), 119.5 (C2''), 119.2 (C5'), 26.7 ($CO\underline{C}H_3$) ppm; MS (ESI): *m/z* (rel intensity): 324 (MH^+, 30), 191 (2), 190 (7), 189 (100); HRMS (ESI-TOF): calcd for $C_{17}H_{14}N_3O_2S$ [MH^+]: 324.0801; found: 324.0801.

***N*-(3-Cyanophenyl)-2-(pyrimidin-2-yl)thiophene-3-carboxamide (3p).** According to the General Procedure, **1a** (0.5 mmol, 81.2 mg) was treated with 3-cyanophenyl isocyanate **2p** (1.0 mmol,152.8 mg), $Cp^*Co(CO)I_2$ (0.012 mmol, 7.5 mg), $AgSbF_6$ (0.05 mmol, 18.3 mg), $NaOPiv{\cdot}H_2O$ (0.05 mmol, 6.9 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 50:50:1), **3p** was obtained as a white solid (53 mg, 32%): mp (CH_2Cl_2): 222-225 ºC; IR (ATR): 3080, 1666 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.90 (d, *J* = 4.9 Hz, 2H, H4', H6'), 8.12 (t, *J* = 2.0 Hz, 1H, H2''), 8.06 (ddd, *J* = 8.7, 2.0,1.4 Hz, 1H, H6'') 7.99 (d, *J* = 5.4 Hz, 1H, H4), 7.56 – 7.46 (m, 2H, H5, H5''), 7.43 (dt, *J* = 7.7, 1.4 Hz, 1H, H4''), 7.38 (t, *J* = 4.9 Hz, 1H, H5') ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 160.8, 160.7 (C=O, C2'), 156.7 (C4', C6'), 140.9 (C2), 139.9 (C3), 137.6 (C1''), 135.0 (C4''), 129.9 (C4), 128.9 (C2''), 127.2 (C5''), 124.3 (C6''), 123.3 (C5), 119.3 (C5'), 118.7 (CN), 113.0 (C3'') ppm; MS (ESI): *m/z* (rel intensity): 307 (MH^+, 26), 191 (3), 190 (7), 189 (100); HRMS (ESI-TOF): calcd for $C_{16}H_{11}N_4OS$ [MH^+]: 307.0648; found: 307.0653.



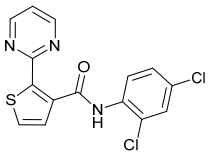
***N*-(3-Methoxyphenyl)-2-(pyrimidin-2-yl)thiophene-3-carboxamide (3q).** According to the General Procedure, **1a** (0.5 mmol, 82.1 mg) was treated with 3-methoxyphenyl isocyanate **2q** (1.01 mmol, 0.13 mL), $Cp^*Co(CO)I_2$ (0.013 mmol, 6.5 mg), $AgSbF_6$ (0.05 mmol, 20.1 mg), $NaOPiv{\cdot}H_2O$ (0.05 mmol, 6.5 mg) in DCE (2 mL).



After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 60:40:1), **3q** was obtained as a white solid (54.6 mg, 35%): mp (CH_2Cl_2): 116-119 ºC; IR (ATR): 3095, 1662 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.83 (d, *J* = 4.9 Hz, 2H, H4', H6'), 7.96 (d, *J* = 5.4 Hz, 1H, H4), 7.62 (t, *J* = 2.0 Hz, 1H, H2''), 7.46 (d, *J* = 5.4 Hz, 1H, H5), 7.33 – 7.24 (m, 2H, H5', H6''), 7.22-7.19 (m, 1H, H5''), 6.70 (ddd, *J* = 8.1 2.2, 1.5 Hz, 1H, H4''), 3.86 (s, 3H, OCH_3) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 160.8, 160.5 (C=O, C2'), 160.2 (C3''), 156.6 (C4', C6'), 140.4,140.3 (C2, C3), 138.4 (C1''), 134.9 (C4), 129.6 (C5''), 128.5 (C5), 119.1 (C5'), 112.4 (C4''), 109.8 (C6''), 105.9 (C2''), 55.3 (OCH_3) ppm; MS (ESI): *m/z* (rel intensity): 312 (MH^+, 24), 191 (3), 190 (7), 189 (100); HRMS (ESI-TOF): calcd for $C_{16}H_{14}N_3O_2S$ [MH^+]: 312.0801; found: 312.0808.

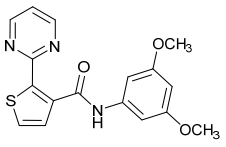
***N*-(2-Nitrophenyl)-2-(pyrimidin-2-yl)thiophene-3-carboxamide (3r).** According to the General Procedure, **1a** (0.52 mmol, 85.3 mg) was treated with 2-nitrophenyl isocyanate **2r** (1.04 mmol, 164.3 mg), Cp*Co(CO)I_2 (0.03 mmol, 14.5 mg), $AgSbF_6$ (0.077 mmol, 26.3 mg), NaOPiv·H_2O (0.061 mmol, 7.6 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 70:30:1), **3r** was obtained as a white solid (111.6 mg, 65%): mp (CH_2Cl_2): 161-164 ºC; IR (ATR): 3076, 1658 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.78 (d, *J* = 4.9 Hz, 2H, H4', H6'), 8.53 (dd, *J* = 8.4, 1.3 Hz, 1H, H6''), 8.08 (dd, *J* = 8.4, 1.3 Hz, 1H, H3'), 7.76 (d, *J* = 5.3 Hz, 1H, H4), 7.73 – 7.63 (m, 1H, H5''), 7.49 (d, *J* = 5.3 Hz, 1H, H5), 7.29 – 7.22 (m, 2H, H5', H4'') ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 162.9 (CO), 160.4 (C2'), 157.0 (C4', C6'), 141.7, 140.3 (C2, C2'') 137.1 (C3), 134.4 (C5), 133.4 (C1''), 133.1 (C5''), 128.7 (C3''), 125.4, 125.1, 124.1 (C4'', C4, C6''), 119.2 (C5') ppm; MS (ESI): *m/z* (rel intensity): 349 (MNa^+, 42), 327 (MH^+, 16), 245 (3), 209 (2), 191 (3), 190 (3), 189 (100), 177 (9); HRMS (ESI-TOF): calcd for $C_{15}H_{11}N_4O_3S$ [MH^+]: 327.0546; found: 327.0555.

***N*-(2,4-Dichlorophenyl)-2-(pyrimidin-2-yl)thiophene-3-carboxamide (3s).** According to the



General Procedure, **1a** (0.5 mmol, 82.1 mg) was treated with 2,4-dichlorophenyl isocyanate **2s** (1.0 mmol, 188 mg), Cp*Co(CO)I_2 (0.025 mmol, 11.8 mg), $AgSbF_6$ (0.05 mmol, 20.1 mg), NaOPiv·H_2O (0.05 mmol, 6.5 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 90:10:1), **3s** was obtained as a white solid (88 mg, 50%): mp (CH_2Cl_2): 179-181 ºC; IR (ATR): 3094, 1602 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.84 (d, J = 5.0 Hz, 2H, H4', H6'), 8.35 (d, J = 8.9 Hz, 1H, H6''), 7.96 (d, J = 5.4 Hz, 1H, H5), 7.50 (d, J = 5.4 Hz, 1H, H4), 7.46 (d, J = 2.4 Hz, 1H, H3'', 7.36 – 7.27 (m, 2H, H5', H5'') ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 161.3, 160.5 (CO, C2'), 156.9 (C4', C6'), 141.3 (C2), 137.4 (C3), 134.9 (C4), 134.7 (C1''), 129.4 (C4''), 129.0, 128.4 (C3'', C6''), 127.5 (C5), 125.3 (C5''), 125.2 (C2''), 119.1 (C5') ppm; MS (EI): *m/z* (rel intensity): 351 (M^++2, 1), 349 (M^+,3), 314 (1), 189 (100), 161 (9), 135 (15); HRMS (ESI-TOF): calcd for $C_{15}H_{10}Cl_2N_3OS$ [MH^+]: 349.9916; found: 349.9926.

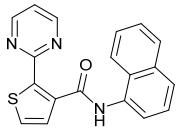
***N*-(3,5-dimethoxyphenyl)-2-(pyrimidin-2-yl)thiophene-3-carboxamide (3t).** According to the



General Procedure, **1a** (0.49 mmol, 81.1 mg) was treated with 3,5-dimethoxyphenyl isocyanate **2t** (1.01 mmol, 148.4 mg), Cp*Co(CO)I_2 (0.025 mmol, 11.8 mg), $AgSbF_6$ (0.052 mmol, 18.0 mg), NaOPiv·H_2O (0.05 mmol, 6.5 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 60:40:1), **3t** was obtained as a white solid (89.4 mg, 53%): mp (CH_2Cl_2): 176-179 ºC; IR (ATR): 3073, 1660 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.88 (d, J = 4.9 Hz, 2H, H4', H6'), 7.98 (d, J = 5.4 Hz, 1H, H4), 7.49 (d, J = 5.4 Hz, 1H, H5), 7.32 (t, J = 4.9 Hz, 1H, H5'), 7.07 (d, J = 2.2 Hz, 2H, H2'', H6''), 6.30 (t, J = 2.2 Hz, 1H, H4''), 3.86 (s, 6H, 2 x CH_3) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 161.0, 160.9 (C=O, C2'), 160.6 (C3'', C5''), 156.6 (C4', C6'), 140.8 (C2), 138.4 (C3), 134.9 (C1''), 131.0 (C4), 128.5 (C5), 119.1 (C5'), 98.6 (C2'', C6''), 96.3 (C4''), 55.4 (2 x -OCH_3) ppm; MS

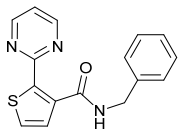
(ESI): *m/z* (rel intensity): 342 (MH^+, 44), 191 (3), 190 (7), 189 (100); HRMS (ESI-TOF): calcd for $C_{17}H_{16}N_3O_3S$ [MH^+]: 342.0907; found: 342.0911.

***N*-(Naphthalen-1-yl)-2-(pyrimidin-2-yl)thiophene-3-carboxamide (3u).** According to the



General Procedure, **1a** (0.5 mmol, 85.7 mg) was treated with naphthalen-1-yl isocyanate **2u**(0.9 mmol, 0.15 mL), Cp*Co(CO)I_2 (0.012 mmol, 5.9 mg), $AgSbF_6$ (0.05 mmol, 19.0 mg), NaOPiv·H_2O (0.05 mmol, 6.8 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 80:20:1), **3u** was obtained as a white solid (40.2 mg, 21%): mp (CH_2Cl_2): 186-189 ºC; IR (ATR): 3271, 1655 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.78 (d, *J* = 4.9 Hz, 2H, H4', H6'), 8.33 – 8.27 (m, 1H, H5''), 8.23 (d, *J* = 7.5 Hz, 1H, H8''), 8.09 (d, *J* = 5.3 Hz, 1H, H4), 7.93 (dd, *J* = 6.3, 3.3 Hz, 1H, H6''), 7.74 (d, *J* = 7.5 Hz, 1H, H4''), 7.58 – 7.50 (m, 4H, H5, H3'', H7'', H2''), 7.28 (t, *J* = 4.9 Hz, 1H, H5') ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 161.2, 160.9 (C=O, C2'), 156.8 (C4', C6'), 140.7 (C2), 138.4 (C1''), 135.3 (C4), 134.3 (C4a''), 133.8 (C3), 128.7, 128.5 (C5'', C3''), 127.8 (C8a''), 126.1, 125.9, 125.7 (C7'', C5, C6''), 125.1 (C8''), 121.8 (C4''), 120.9 (C5'), 119.1 (C2'') ppm; MS (ESI): *m/z* (rel intensity): 332 (MH^+, 36), 191 (2), 190 (7), 189 (100); HRMS (ESI-TOF): calcd for $C_{19}H_{14}N_3OS$ [MH^+]: 332.0852; found: 332.0855.

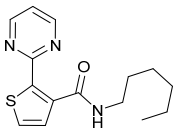
***N*-Benzyl-2-(pyrimidin-2-yl)thiophene-3-carboxamide (3v).** According to the General



Procedure, **1a** (0.5 mmol, 81.2 mg) was treated with benzyl isocyanate **2v** (1.06 mmol, 0.13 mL), Cp*Co(CO)I_2 (0.025 mmol, 11.9 mg), 0.05 mmol, 17.5 mg), NaOPiv·H_2O (0.05 mmol, 6.4 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 60:40:1), **3v** was obtained as a brown solid (83.4 mg, 56%): mp (CH_2Cl_2): 85-87 ºC; IR (ATR): 3037, 1644 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 11.52 (broad s, 1H, NH), 8.48 (d, *J* = 4.9 Hz, 2H, H4', H6'), 7.91 (d, *J* = 5.3 Hz, 1H, H4), 7.49 – 7.31 (m, 6H, H5, Ph), 7.13 (t, *J* = 4.9 Hz, 1H, H5'), 4.68 (d, *J* = 4.9 Hz, 2H, CH_2) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 162.7, 160.7 (C=O, C2'), 156.4 (C4', C6'), 140.5 (C2), 138.5 (C3), 137.8 (C1''),

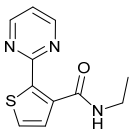
134.5 (C4), 128.6 , 128.3 (C2'', C3''', C5'', C6''), 128.2 (C4''), 127.3 (C5), 118.8 (C5'), 44.5 (CH_2) ppm; MS (ESI): *m/z* (rel intensity): 296 (MH^+, 100), 274 (20), 250 (6), 189 (77) ; HRMS (ESI-TOF): calcd for $C_{16}H_{14}N_3OS$ [MH^+]: 296.0852; found: 296.0853.

***N*-Hexyl-2-(pyrimidin-2-yl)thiophene-3-carboxamide (3w).** According to the General



Procedure, **1a** (0.5 mmol, 81.4 mg) was treated with hexyl isocyanate **2w** (1.03 mmol, 0.15 mL), Cp*Co(CO)I_2 (0.012 mmol, 5.9 mg), $AgSbF_6$ (0.052 mmol, 18.1 mg), NaOPiv·H_2O (0.05 mmol, 7.2 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 50:50:1), **3w** was obtained as a yellow solid (56 mg, 39%): mp (CH_2Cl_2): 57-60 ºC; IR (ATR): 3232, 1640 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 10.73 (broad s, 1H, NH), 8.68 (d, *J* = 4.9 Hz, 2H, H4', H6'), 7.77 (d, *J* = 5.4 Hz, 1H, H4), 7.34 (d, *J* = 5.4 Hz, 1H, H5), 7.17 (t, *J* = 4.9 Hz, 1H, H5'), 3.40 (td, *J* = 7.0, 5.2 Hz, 2H, 2 x H1''), 1.66-1.52 (m, 2H, 2 x H2''), 1.37 – 1.23 (m, 6H, 2 x H3'', 2 x H4'', 2 x H5''), 0.86 – 0.78 (m, 3H, CH_3) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 162.9, 161.1 (C2', C=O), 156.6 (C4', C6'), 140.1 (C3), 138.3 (C2), 134.4 (C4), 128.3 (C5), 118.8 (C5'), 39.9, 31.6, 29.3, 27.0, 22.6 (CH_2), 14.0 (CH_3) ppm; MS (ESI): *m/z* (rel intensity): 290 (MH^+, 100), 190 (3), 189 (52); HRMS (ESI-TOF): calcd for $C_{15}H_{20}N_3OS$ [MH^+]: 290.1322; found: 290.1324.

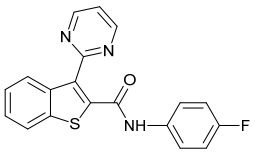
***N*-Ethyl-2-(pyrimidin-2-yl)thiophene-3-carboxamide (3x).** According to the General Procedure,



1a (0.49 mmol, 80.5 mg) was treated with ethyl isocyanate **2x** (1.0 mmol, 0.08 mL), Cp*Co(CO)I_2 (0.012 mmol, 7.6 mg), $AgSbF_6$ 0.053 mmol, 18.5 mg), NaOPiv·H_2O (0.053 mmol, 7.6 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 60:40:1), **3x** was obtained as a white solid (23 mg, 21%): mp (CH_2Cl_2): 150-153 ºC; IR (ATR): 3292, 1640 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 10.76 (broad s, 1H, NH), 8.77 (d, *J* = 4.9 Hz, 2H, H4', H6'), 7.85 (d, *J* = 5.3 Hz, 1H, H4), 7.43 (d, *J* = 5.3 Hz, 1H, H5), 7.25 (t, *J* = 4.9 Hz, 1H, H5'), 3.59-3.44 (m, 2H, CH_2), 1.32 (t, *J* = 7.3 Hz, 3H, CH_3) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 162.9, 161.0 (C2', C=O), 156.5 (C4', C6'), 140.1 (C3), 138.2 (C2), 134.3 (C4), 128.3

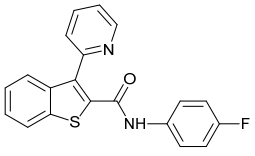
(C4), 118.9 (C5'), 34.6 (CH_2), 14.5 (CH_3) ppm; MS (ESI): *m/z* (rel intensity): 234 (MH^+, 50), 191 (3), 190 (7), 189 (100); HRMS (ESI-TOF): calcd for $C_{11}H_{12}N_3OS$ [MH^+]: 234.0696; found: 234.0699.

***N*-(4-Fluorophenyl)-3-(pyrimidin-2-yl)benzo[*b*]thiophene-2-carboxamide (5aa).** According to



the General Procedure, **4a** (0.5 mmol, 106.1 mg) was treated with 4-fluorophenyl isocyanate **2a** (1.0 mmol, 0.11 mL), Cp*Co(CO)I_2 (0.025 mmol, 12 mg), $AgSbF_6$ (0.05 mmol, 17.1 mg), NaOPiv·H_2O (0.05 mmol, 6.2 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 80:20:1), **5aa** was obtained as a white solid (123.3 mg, 71%): mp (CH_2Cl_2): 147-149 ºC; IR (ATR): 3058, 1651 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.06 (d, *J* = 4.9 Hz, 2H, H4', H6'), 8.35 – 8.23 (m, 1H, H4), 8.00 – 7.88 (m, 1H, H7), 7.70 (dd, *J* = 8.7, 5.0 Hz, H2'', H6''), 7.56 – 7.40 (m, 3H, H5', H5, H6), 7.08 (t, *J* = 8.7 Hz, 2H, H3'', H5'') ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 162.2, 160.3 (C2', C=O), 159.4 (d, *J* = 242.2 Hz, C4''), 156.9 (C4', C6'), 143.6 (C7a), 139.5 (C3), 134.4 (C2), 130.9 (C3a), 126.4 (C5), 125.8 (C6), 125.2 (C4), 122.8 (d, *J* = 2.5 Hz, C1''), 122.2 (C7), 121.5 (d, *J* = 8.3 Hz, C2'', C6''), 119.8 (C5'), 115.8 (d, *J* = 22.5 Hz, C3'', C5'') ppm; ^{19}F NMR (282 MHz, $CDCl_3$) -117.64 ppm; MS (ESI): *m/z* (rel intensity): 350 (MH^+, 31), 241 (3), 240 (10), 239 (100); HRMS (ESI-TOF): calcd for $C_{19}H_{13}FN_3OS$ [MH^+]: 350.0758; found: 350.0761.

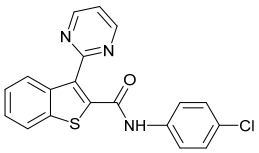
***N*-(4-Fluorophenyl)-3-(pyridin-2-yl)benzo[*b*]thiophene-2-carboxamide (5ba).** According to the



General Procedure, **4b** (0.5 mmol, 105.6 mg) was treated with 4-fluorophenyl isocyanate **2a** (1.0 mmol, 0.12 mL), Cp*Co(CO)I_2 (0.025 mmol, 12 mg), $AgSbF_6$ (0.05 mmol, 17.1 mg), NaOPiv·H_2O (0.05 mmol, 6.2 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 80:20:1), **5ba** was obtained as a white solid (169 mg, 97%): mp (CH_2Cl_2): 159-160 ºC; IR (ATR): 3060, 1647 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 11.92 (s, 1H, NH), 8.90 (d, *J* = 4.6 Hz, 1H, H6'), 8.04 – 7.91 (m, 2H, H4, H7), 7.73 (d, *J* = 8.3 Hz, 2H, H2'', H6''), 7.70 – 7.62 (m, 2H, H3', H4'), 7.57 – 7.38 (m, 3H, H5', H5, H6), 7.05 (t, *J* = 8.7 Hz, 2H, H3'', H5'') ppm; $^{13}C\{^1H\}$ NMR

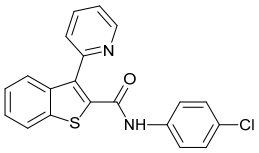
(75.5 MHz, $CDCl_3$) δ 160.5 (C=O), 159.5 (d, J = 242.2 Hz, C4''), 153.2 (C2'), 148.6 (C7a), 140.4 (C3), 139.8 (C6'), 139.5 (C2), 137.5 (C4'), 134.5 (d, J = 2.2 Hz, C1''), 133.2 (C3a), 127.0 (C6), 126.4 (C5), 125.0 (C5'), 124.1 (C4), 123.7 (C7), 122.7 (C3'), 121.3 (d, J = 7.5 Hz, C2'', C6''), 115.6 (d, J = 22.5 Hz, C3'', C5'') ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ -118.01 ppm; MS (ESI): *m/z* (rel intensity): 349 (MH^+, 100), 301 (2), 241 (3), 240 (3), 239 (10), 238 (88); HRMS (ESI-TOF): calcd for $C_{20}H_{14}FN_2OS$ [MH^+]: 349.0805; found: 349.0809.

***N*-(4-Chlorophenyl)-3-(pyrimidin-2-yl)benzo[*b*]thiophene-2-carboxamide (5ab).** According to



the General Procedure, **4a** (0.5 mmol, 106.1 mg) was treated with 4-chlorophenyl isocyanate **2c** (1.0 mmol, 153.6 mg), Cp*Co(CO)I_2 (0.025 mmol, 12 mg), $AgSbF_6$ (0.05 mmol, 17.1 mg), NaOPiv·H_2O (0.05 mmol, 6.2 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 90:10:1), **5ab** was obtained as a white solid (130 mg, 74%): mp (CH_2Cl_2): 198-199 ºC; IR (ATR): 3075, 1644 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.07 (d, J = 5.0 Hz, 2H, H4', H6'), 8.34 – 8.27 (m, 1H, H4), 7.97 – 7.92 (m, 1H, H7), 7.72 – 7.66 (m, 2H, H2'', H6''), 7.54 – 7.44 (m, 3H H5', H5, H6), 7.38 – 7.32 (m, 2H, H3'', H5'') ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 162.2 (C2'), 160.4 (C=O), 157.0 (C4', C6'), 143.6 (C7a), 139.6 (C3), 136.9 (C2), 131.0 (C3a), 129.3 (C4''), 129.1 (C3'', C5''), 126.5(C5), 126.0 (C6), 125.2 (C4, C1''), 122.2 (C7), 121.2 (C2``, C6``), 119.9 (C5') ppm; MS (ESI): *m/z* (rel intensity): 368 (MH^++2, 8), 366 (MH^+, 26), 281 (2), 241 (3), 240 (10), 239 (100); HRMS (ESI-TOF): calcd for $C_{19}H_{13}ClN_2OS$ [MH^+]: 366.0462; found: 366.0475.

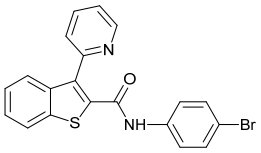
***N*-(4-Chlorophenyl)-3-(pyridin-2-yl)benzo[*b*]thiophene-2-carboxamide (5bb).** According to the



General Procedure, **4b** (0.5 mmol, 105.6 mg) was treated with 4-chlorophenyl isocyanate **2c** (1.0 mmol, 153.6 mg), Cp*Co(CO)I_2 (0.025 mmol, 12 mg), $AgSbF_6$ (0.05 mmol, 17.1 mg), NaOPiv·H_2O (0.05 mmol, 6.2 mg) in DCE (2 mL).After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 70:30:1), **5bb** was obtained as a brown solid (173.2 mg, 95%): mp (CH_2Cl_2):

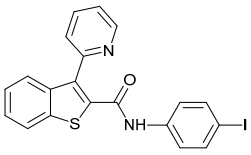
180-182 ºC; IR (ATR): 3080, 1651 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 12.04 (s, 1H, NH), 8.89 (d, J = 4.3 Hz, 1H, H6'), 8.03 – 7.93 (m, 2H, H4, H4'), 7.73-7.71 (m, 2H, H3', H7), 7.68 – 7.62 (m, 2H, H2``, H6``), 7.54 – 7.39 (m, 3H, H5, H6, H5`), 7.31 (m, 2H, H3'', H5'') ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 160.7 (C=O), 153.2 (C2'), 148.6 (C6'), 140.4, 139.8 (C7a, C3a), 139.5 (C2), 137.6 (C4'), 137.1 (C1''), 133.3 (C4'', C3), 129.0 (C3'', C5''), 127.1 (C5'), 126.5 (C5), 125.1 (C6), 124.2 (C7), 123.8 (C4), 122.7 (C3'), 120.9 (C2'', C6'') ppm; MS (ESI): *m/z* (rel intensity): 367 (MH^++2, 31), 365 (MH^+, 98), 341 (8), 310 (1), 309 (6), 240 (4), 239 (12), 238 (100); HRMS (ESI-TOF): calcd for $C_{20}H_{14}ClN_2OS$ [MH^+]: 365.0510; found: 365.0519.

***N*-(4-Bromophenyl)-3-(pyridin-2-yl)benzo[*b*]thiophene-2-carboxamide (5bc).** According to the



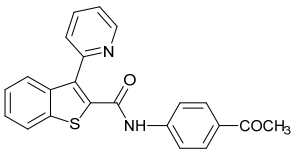
General Procedure, **4b** (0.5 mmol, 105.6 mg) was treated with 4-bromophenyl isocyanate **2h** (1.0 mmol, 198.0 mg), Cp*Co(CO)I_2 (0.025 mmol, 12 mg), $AgSbF_6$ (0.05 mmol, 17.1 mg), NaOPiv·H_2O (0.05 mmol, 6.2 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 80:20:1), **5bc** was obtained as a white solid (191 mg, 93%): mp (CH_2Cl_2): 177-178 ºC; IR (ATR): 3060, 1647 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 12.04 (s, 1H, NH), 8.95 – 8.83 (m, 1H, H6'), 8.04 – 7.92 (m, 2H, H4, H4'), 7.75 – 7.70 (m, 2H, H3', H7), 7.62 – 7.57 (m, 2H, H2'',H6''), 7.54 – 7.39 (m, 5H, H3'', H5'', H5, H6, H5') ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 160.7 (C=O), 153.2 (C2'), 148.6 (C6'), 140.4, 139.9, 139.5 (C7a, C3, C2), 137.6 (C4'), 137.5 (C1''), 133.3(C3a), 132.0 (C3'', C5''), 127.1 (C5'), 126.5 (C5), 125.1 (C6), 124.2 (C7), 123.8 (C4), 122.7 (C3'), 121.3 (C6'', C2``), 116.7 (C4'') ppm; MS (ESI): *m/z* (rel intensity): 411 (MH^++2, 100), 409 (MH^+, 98), 240 (3), 239 (11), 238 (97); HRMS (ESI-TOF): calcd for $C_{20}H_{14}BrN_2OS$ [MH^+]: 409.0005; found: 409.0012.

***N*-(4-Iodophenyl)-3-(pyridin-2-yl)benzo[*b*]thiophene-2-carboxamide (5bd).** According to the



General Procedure, **4b** (0.5 mmol, 105.6 mg) was treated with 4-iodophenyl isocyanate **2i** (1.0 mmol, 245 mg), Cp*Co(CO)I_2 (0.025 mmol, 12 mg), $AgSbF_6$ (0.05 mmol, 17.1 mg), NaOPiv·H_2O (0.05 mmol, 6.2 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 80:20:1), **5bd** was obtained as a white solid (244 mg, 89%): mp (CH_2Cl_2): 168-170 ºC; IR (ATR): 3080, 1644 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 12.04 (s, 1H, NH), 8.88 (d, J = 4.1 Hz, 1H, H6'), 8.02 – 7.93 (m, 2H, H4, H4'), 7.75-7.70 (m, 2H, H3', H7), 7.68 – 7.62 (m, 2H, H2'', H6''), 7.54 – 7.39 (m, 5H, H3'', H5'', H6 ,H5, H5') ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 160.7 (C=O), 153.2 (C2'), 148.6 (C6'), 140.4, 139.9, 139.5 (C7a, C3, C2), 138.2 (C1''), 137.9 (C5'', C3''), 137.6 (C4'), 133.4 (C3a), 127.1 (C5`), 126.5 (C5), 125.1 (C6), 124.2 (C7), 123.8 (C4), 122.7 (C3`), 121.6 (C6'', C2''), 87.3 (C4'') ppm; MS (ESI): *m/z* (rel intensity): 456 (MH^+, 100), 413 (7), 346 (4), 239 (5), 238 (41); HRMS (ESI-TOF): calcd for $C_{20}H_{14}IN_2OS$ [MH^+]: 456.9866; found: 456.9875.

***N*-(4-Acetylphenyl)-3-(pyridin-2-yl)benzo[*b*]thiophene-2-carboxamide (5be).** According to the



General Procedure, **4b** (0.5 mmol, 105.6 mg) was treated with 4-acetylphenyl isocyanate **2f** (1.0 mmol, 161.2 mg), Cp*Co(CO)I_2 (0.025 mmol, 12 mg), $AgSbF_6$ (0.05 mmol, 17.1 mg), NaOPiv·H_2O (0.05 mmol, 6.2 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 70:30:1), **5be** was obtained as a white solid (161.4 mg, 87%): mp (CH_2Cl_2): 194-195 ºC; IR (ATR): 3090, 1679, 1658 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.93 (d, J = 5.0 Hz, 1H, H6`), 8.04 – 7.95 (m, 4H, H4, H4', H5'', H3''), 7.82 – 7.71 (m, 4H, H7, H6'', H2'', H3'), 7.57 – 7.40 (m, 3H, H6, H5', H5), 2.60 (s, 3H, CH_3) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 196.9 ($\underline{C}OCH_3$), 161.0 (CO), 153.1 (C2'), 148.6 (C6'), 142.8(C1''), 140.1, 140.0, 139.5 (C7a, C3, C2), 137.7 (C4''), 133.6 (C3a), 132.8 (C4'), 129.8 (C5'', C3''), 127.1(C5'), 126.6 (C5), 125.2 (C6), 124.3(C7), 123.9(C4), 122.7(C3'), 119.1(C2'', C6''), 26.4 ($CO\underline{C}H_3$) ppm; MS (ESI): *m/z* (rel intensity): 373 (MH^+, 100), 326

(4), 319 (4), 239 (8), 238 (66); HRMS (ESI-TOF): calcd for $C_{22}H_{17}N_2O_2S$ [MH^+]: 373.1005; found: 373.1009.

***N*-Phenyl-3-(pyridin-2-yl)benzo[*b*]thiophene-2-carboxamide (5bf).** According to the General Procedure, **4b** (0.5 mmol, 105.6 mg) was treated with phenyl isocyanate **2b** (1.0 mmol, 0.110 mL), Cp*Co(CO)I_2 (0.025 mmol, 12 mg), $AgSbF_6$ (0.05 mmol, 17.1 mg), NaOPiv·H_2O (0.05 mmol, 6.2 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt 80:20), **5bf** was obtained as a white solid (138 mg, 84%): mp (CH_2Cl_2): 124-125 ºC; IR (ATR): 3080, 1708 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 11.73 (s, 1H, NH), 8.82 (d, J = 5.0 Hz, 1H, H6'), 7.88-7.85 (m, 2H, H4, H4'), 7.63-7.58 (m, 3H, H2'', H6'', H7), 7.40 – 7.18 (m, 6H, H3'', H5'', H3', H6, H5, H5'), 7.03 (t, J = 7.3 Hz, 1H, H4'') ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 160.6 (CONH), 153.3 (C2'), 148.8 (C6'), 139.8, 139.6, 138.5 (C7a, C3, C2), 137.5 (C4'), 133.2 (C3a), 130.5 (C1''), 129.8 (C5'), 129.1 (Ph), 126.9, 126.4 (C5, C6), 125.0 (C7), 124.2, 124,1, 123.7 (C4, C3', C5'), 122.7, 120.7, 119.8 (Ph) ppm; MS (ESI): *m/z* (rel intensity): 331 (MH^+, 61), 301 (5), 240 (3), 239 (12), 238 (100), 213 (15), 149 (15); HRMS (ESI-TOF): calcd for $C_{20}H_{15}N_2O_2S$ [MH^+]: 331.0900; found: 331.0906.

***N*-(3-Acetylphenyl)-3-(pyridin-2-yl)benzo[*b*]thiophene-2-carboxamide (5bg).** According to the General Procedure, **4b** (0.5 mmol, 105.6 mg) was treated with 3-acetylphenyl isocyanate **2o** (1.0 mmol, 0.15 mL), Cp*Co(CO)I_2 (0.025 mmol, 12 mg), $AgSbF_6$ (0.05 mmol, 17.1 mg), NaOPiv·H_2O (0.05 mmol, 6.2 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 70:30:1), **5bg** was obtained as a brownish solid (181,6 mg, 98%): mp (CH_2Cl_2): 139-140 ºC; IR (ATR): 3075, 1683 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.95 (d, J = 5.0 Hz, 1H, H6'), 8.27 (t, J = 2.0 Hz, 1H, H2''), 8.03 – 7.92 (m, 3H, H4, H4'', H6''), 7.72 (m, 3H, H7, H4', H5''), 7.56 – 7.39 (m, 4H, H5, H6, H3', H5'), 2.65 (s, 3H, CH_3) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 197.85 ($\underline{C}OCH_3$), 160.9 (CO), 153.0 (C2'), 148.6 (C6'), 140.2, 139.8, 139.5 (C7a, C3, C2), 138.9 (C1''), 137.8

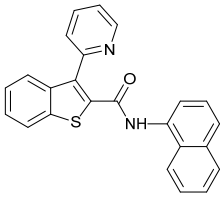
(C3'') , 137.7 (C4'), 133,5. (C3a) 129.3 (C5'), 127.0 (C5''), 126.5 (C4''), 125.1 (C7), 124.3, 124.2 (C6), 123.9 (C5, C6, C4), 123.9 (C6''), 122.7 (C3'), 119.4 (C2''), 26.8 (CH_3) ppm; MS (ESI): *m/z* (rel intensity): 373 (MH^+, 100), 239 (5), 238 (46); HRMS (ESI-TOF): calcd for $C_{22}H_{17}N_2O_2S$ [MH^+]: 373.1005; found: 373.1004..

***N*-(3,5-dimethoxyphenyl)-3-(pyridin-2-yl)benzo[*b*]thiophene-2-carboxamide (5bh).** According to the General Procedure, **4b** (0.5 mmol, 105.6 mg) was treated with 3,5-dimethoxyphenyl isocyanate **2t** (1.0 mmol, 147.2 mg), Cp*Co(CO)I_2 (0.025 mmol, 12 mg), $AgSbF_6$ (0.05 mmol, 17.1 mg), NaOPiv·H_2O (0.05 mmol, 6.2 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 80:20:1), **5bh** was obtained as a pale brown solid (168.4 mg, 86%): mp (CH_2Cl_2): 150-151 ºC; IR (ATR): 3070, 1652 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 11.90 (s, 1H, NH), 8.92 (d, *J* = 5.0, Hz, 1H, H6'), 8.01-7.90 (m, 2H, H4, H7), 7.75 – 7.68 (m, 2H, H4', H5'), 7.56 – 7.36 (m, 3H, H5, H6, H3'), 6.96 (d, *J* = 2.2 Hz, 2H, H2'', H6''), 6.27 (t, *J* = 2.2 Hz, 1H, H4''), 3.83 (s, 6H, OCH_3) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 161.0 (C3'', C5''), 160.7 (CO), 153.2 (C2'), 148.7 (C6'), 140.6, 140.1, 139.8, 139.5 (C7a, C3, C2, C1''), 137.6 (C4'), 133.3 (C3a), 127.0 (C5'), 126.4 (C5), 125.0 (C6), 124.2 (C7), 123.7 (C4), 122.7 (C3`), 98.1 (C6'', C2''), 96.8 (C4''), 55.4 (OCH_3) ppm; MS (ESI): *m/z* (rel intensity): 391 (MH^+, 100), 239 (4), 238 (44); HRMS (ESI-TOF): calcd for $C_{22}H_{19}N_2O_3S$ [MH^+]: 391.1111; found: 391.1121.

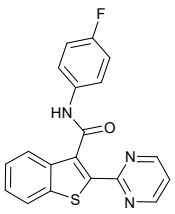
***N*-benzyl-3-(pyridin-2-yl)benzo[*b*]thiophene-2-carboxamide (5bi).** According to the General Procedure, **4b** (0.5 mmol, 105.6 mg) was treated with benzyl isocyanate **2v** (1.0 mmol, 0.124 mL), Cp*Co(CO)I_2 (0.025 mmol, 12 mg), $AgSbF_6$ (0.05 mmol, 17.1 mg), NaOPiv·H_2O (0.05 mmol, 6.2 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 80:20:1), **5bi** was obtained as a white solid (130.7 mg, 76%): mp (CH_2Cl_2): 98-99 ºC; IR (ATR): 3030, 1641 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.53 (broad s, 1H, NH), 8.37 (d, *J* = 5.0, Hz, 1H, H6'), 7.96 – 7.83 (m, 2H, H4, H7), 7.67 – 7.57

(m, 2H, H4', H5'), 7.50 – 7.27 (m, 6H, H5, H6, H3', 3 x Ph), 7.21-7.17 (m, 2H, 2 x Ph), 4.56 (d, *J* = 5.2 Hz, 2H, CH_2) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) *δ* 162.5 (CO), 153.3 (C2'), 148.9 (C6'), 139.6, 139.5, 139.4 (C7a, C3, C2,) 137.7 (C1''), 137.1 (C4`), 133.8 (C3a), 128.6 (Ph), 127.9 (Ph), 127.4 (C5'), 126.5, 126.1 (C5, C6), 124.9 (Ph),124.0 (C7),123.2 (C4), 122.6 (C3'), 44.4 (CH_2) ppm; MS (ESI): *m/z* (rel intensity): 345 (MH^+, 100), 240 (2), 239 (7), 238 (69); HRMS (ESI-TOF): calcd for $C_{21}H_{17}N_2OS$ [MH^+]: 345.1056; found: 345.1065.

***N*-(Naphthalen-1-yl)-3-(pyridin-2-yl)benzo[*b*]thiophene-2-carboxamide (5bj).** According to the General Procedure, **4b** (0.5 mmol, 105.6 mg) was treated with naphthalen-1-yl isocyanate **2u** (1.0 mmol, 0.144 mL), Cp*Co(CO)I_2 (0.025 mmol, 12 mg), $AgSbF_6$ (0.05 mmol, 17.1 mg), NaOPiv·H_2O (0.05 mmol, 6.2 mg) in DCE (2 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 80:20:1), **5bj** was obtained as a white solid (89.7 mg, 47%): mp (CH_2Cl_2): 152-153 ºC; IR (ATR): 3200, 1658 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) *δ* 8.62 (d, *J* = 5.1 Hz, 1H, H6'), 8.25-8.21 (m, 2H, H8'', H5''), 7.96 – 7.74 (m, 3H, H4, H4', H7), 7.78 – 7.68 (m, 3H, H7'', H6'', H4''), 7.53 – 7.27 (m, 6H, H3'', H2'', H5, H6, H5', H6') ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) *δ* 161.2 (CO), 153.2 (C2'), 149.3 (C6'), 140.7, 139.9, 139.7 (C7a, C3, C2), 137.6 (C1''), 134.2 (C4'), 133.6 (C3a), 133.1 (C4a"), 128.7 (C5"), 126.9 (C8a"), 126.8, 126.4, 126.1, 125.9, 125.8 (C7", C6", C3", C5', C8"), 125.1, 125.0 (C5, C6), 124.1 (C7), 123.4 (C4), 122.7 (C3'), 121.3 (C4"), 119.7 (C2") ppm; MS (ESI): *m/z* (rel intensity): 381 (MH^+, 100), 239 (5), 238 (48); HRMS (ESI-TOF): calcd for $C_{24}H_{17}N_2OS$ [MH^+]: 381.1056; found: 381.1066.



***N*-(4-Fluorophenyl)-2-(pyrimidin-2-yl)benzo[*b*]thiophene-3-carboxamide (7a).** According to the General Procedure, **6a** (0.5 mmol, 106 mg) was treated with 4-fluorophenyl isocyanate **2a** (1.0 mmol, 0.11 mL), Cp*Co(CO)I_2 (0.025 mmol, 12 mg), $AgSbF_6$ (0.05 mmol, 17.1 mg), NaOPiv·H_2O (0.05 mmol, 6.2 mg) in DCE (2 mL).. After purification by flash column chromatography (silica gel, petroleum

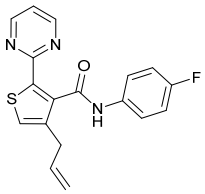


ether/AcOEt/Et_3N 60:40:1), **7a** was obtained as a white solid (97.7 mg, 56%): mp (CH_2Cl_2): 224-226 ºC; IR (ATR): 3250, 1675 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.32 (broad s, 1H, NH), 8.72 (d, *J* = 4.9 Hz, 2H, H4', H6'), 8.14 (dd, *J* = 6.5, 2.8 Hz, 1H, H4), 7.85 – 7.75 (m, 1H, H7), 7.69 – 7.57 (m, 2H, H5, H6), 7.44 – 7.33 (m, 2H, H2'', H6''), 7.15 (t, *J* = 4.9 Hz, 1H, H5'), 6.98-7.06 (m, 2H, H3'',H5'') ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 163.3 (CO), 161.1 (C2'), 159.8 (*J* = 238.5 Hz, C4''), 157.0 (C4', C6'), 140.2, 140.1, 139.5 (C2, C3, C7a), 134.4 (*J* = 2.6 Hz, C1''), 133.1 (C3a), 126.6 (C5), 125.3, 125.0 (C4, C7), 122.1 (C6), 122.0 (*J* = 7.8 Hz, C2'', C6''), 119.4 (C5'), 115.7 (*J* = 22.2 Hz, C3'', C5'') ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ -117.8 ppm; MS (ESI): *m/z* (rel intensity): 350 (MH^+, 10), 241 (3), 240 (10), 239 (100), 189 (1); HRMS (ESI-TOF): calcd for $C_{19}H_{13}FN_3OS$ [MH^+]: 350.0758; found: 350.0766.

***N*-(4-Fluorophenyl)-2-(pyridin-2-yl)benzo[*b*]thiophene-3-carboxamide (7b).** According to the General Procedure, **6b** (0.5 mmol, 105.4 mg) was treated with 4-fluorophenyl isocyanate **2a** (1.0 mmol, 0.11 mL), Cp*Co(CO)I_2 (0.025 mmol, 12 mg), $AgSbF_6$ (0.05 mmol, 17.1 mg), NaOPiv·H_2O (0.05 mmol, 6.2 mg) in DCE (2 mL)After purification by flash column chromatography (silica gel, petroleum ether/AcOEt/Et_3N 80:20:1), **7b** was obtained as a white solid (99.1 mg, 57%): mp (CH_2Cl_2): 213-216 ºC; IR (ATR): 3200, 1666 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 10.43 (s, 1H, NH), 8.57 (dt, *J* = 4.9, 1.4 Hz, 1H, H6'), 8.32 – 8.24 (m, 1H, H4), 7.83 – 7.67 (m, 5H, H5, H6, H7, H3', H4'), 7.50 – 7.38 (m, 2H, H2'', H6''), 7.28 – 7.20 (m, 1H, H5'), 7.16 – 7.04 (m, 2H, H3'', H5'') ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 162.8 (CO), 159.1 (*J* = 241.5 Hz, C4''), 151.8 (C2'), 148.5 (C6'), 141.7, 139.5, 138.8 (C2, C7a, C3), 137.4 (C4'), 134.5 (*J* = 2.1 Hz , C1''), 125.8, 125.2, 125.0, 124.6 (C4, C6, C5, C3'), 123.5 (C7), 121.7 (*J* = 8.2 Hz, C2'', C6''), 121.5 (C3a), 115.8 (*J* = 22.5 Hz, C3'', C5'') ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ -117.87 ppm; MS (ESI): *m/z* (rel intensity): 349 (MH^+, 25), 240 (3), 239 (11), 238 (100); HRMS (ESI-TOF): calcd for $C_{20}H_{14}FN_2OS$ [MH^+]: 349.0805; found: 349.0806.

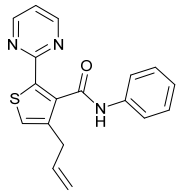
2.4. ITERATIVE FUNCTIONALIZATION REACTIONS.

4-Allyl-*N*-(4-fluorophenyl)-2-(pyrimidin-2-yl)thiophene-3-carboxamide (8a). Under argon



atmosphere, a sealable reaction tube (10 mL, 1.3 × 9 cm) equipped with a stirring bar was charged with **3a** (0.4 mmol, 119.7 mg), Cp*Co(CO)I_2 (0.02 mmol, 9.6 mg), $AgSbF_6$ (0.4 mmol, 137.4 mg), potassium benzoate (0.05 mmol, 7.7 mg) and methyl 4-(allyloxy)benzoate (0.6 mmol, 115.3 mg) in DCE (2 mL). The reaction tube was sealed and heated at 80 °C for 16 h. After cooling to room temperature, the mixture was filtered through silica gel and eluted with ethyl acetate. The solvent was evaporated under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether/EtO_2 8/2) affording **8a** as a white solid (104.8 mg, 77%): mp (CH_2Cl_2): 145-148 ºC; IR (ATR): 3280, 1665 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.70 (broad s, 1H, NH), 8.66 (d, J = 4.9 Hz, 2H, H4', H6'), 7.68–7.50 (m, 2H, H2'', H6''), 7.19–6.96 (m, 4H, H5', H5, H3'', H5''), 6.02 (ddt, J = 16.8, 10.1, 6.7 Hz, 1H,$CH_2C\underline{H}=CH_2$), 5.32 – 5.00 (m, 2H, $CH_2CH=C\underline{H}_2$), 3.56-3.52 (m, 2H, $C\underline{H}_2CH=CH_2$) ppm; ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$) δ 164.5 (CO), 160.8 (C2´), 160.0 (d, J = 243.6 Hz, C4''), 157.1 (C4', C6´), 141.9, 140.3 (C2, C3), 137.9 (C4), 135.9 ($CH_2\underline{C}H=CH_2$), 134.26 (d, J = 2.8 Hz, C1''), 126.1 (C5), 122.0 (d, J = 8.0 Hz, C2'', C6''), 118.9 (C5´), 116.7 ($CH_2CH=\underline{C}H_2$), 115.67 (d, J = 22.5 Hz, C3'', C5''), 33.8 ($\underline{C}H_2CH=CH_2$) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ -117.9 ppm; MS (ESI): *m/z* (rel intensity): 340 (MH+, 15), 230 (10), 229 (100), 158 (4) ; HRMS (ESI-TOF): calcd for $C_{18}H_{15}FN_3OS$ [MH^+]: 340.0914; found, 340.0921.

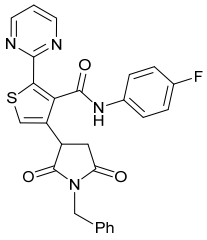
4-Allyl-*N*-4-phenyl)-2-(pyrimidin-2-yl)thiophene-3-carboxamide (8b). Under argon



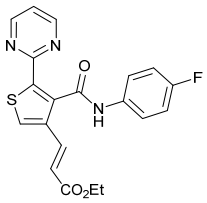
atmosphere, a sealable reaction tube (10 mL, 1.3 × 9 cm) equipped with a stirring bar was charged with **3b** (0.4 mmol, 112.5 mg), $[Cp^*CoI_2]_2$ (0.02 mmol, 17.9 mg), $AgBF_4$ (0.16 mmol, 31.1 mg), AcOH (0.16 mmol, 9.2 µL,) and allylmethyl carbonate (1.2 mmol, 0.14 mL) in TFE (5 mL). The reaction tube was sealed and heated at 70 °C for 16 h. After cooling to room temperature, the mixture was filtered through silica gel and eluted with ethyl acetate. The solvent was evaporated under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether/EtO_2 8/2) affording **8b** as a white solid (104.4 mg, 81%): mp (CH_2Cl_2): 125-127 ºC; IR (ATR): 3282, 1665 cm^{-1}; ^{1}H NMR (300 MHz, acetone-d_6) δ 9.47 (s, 1H, NH), 8.68 (d, J = 4.9 Hz, 2H, H4´,H6´), 7.82 – 7.71 (m, 2H, H2'', H6''), 7.39 – 7.31 (m, 3H, H3'', H5'', H5), 7.27 (t, J = 4.9 Hz, 1H, H5´), 7.15 – 7.04 (m, 1H, H4''), 6.04 (ddt, J = 17.0, 10.0, 6.8 Hz, 1H, $CH_2C\underline{H}=CH_2$), 5.18-5.02 (m, 2H, $CH_2CH=C\underline{H}_2$), 3.50-3.47 (m, 2H, $C\underline{H}_2CH=CH_2$) ppm; ^{13}C{^{1}H} NMR (75.5 MHz, acetone-d_6) δ 164.3 (CO), 160.7 (C2'), 157.2 (C4',C6'), 141.1, 139.9, 139.8, 139.2 (C2, C3, C1'', C4), 136.1 (C

$CH_2\underline{C}H=CH_2$), 128.6 (C3'', C5''), 125.5 (C4''), 123.4 (C5), 119.9 (C2'', C6''), 119.1 (C5´), 115.7 ($CH_2CH=\underline{C}H_2$), 33.3 ($\underline{C}H_2CH=CH_2$) ppm; MS (ESI): *m/z* (rel intensity): 322 (MH^+, 9), 230 (10), 229 (100), 189 (10); HRMS (ESI-TOF): calcd for $C_{18}H_{16}N_3OS$ [MH^+]: 322.1009; found, 322.1009.

4-(1-Benzyl-2,5-dioxopyrrolidin-3-yl)-*N*-(4-fluorophenyl)-2-(pyrimidin-2-yl)thiophene-3-carboxamide (9a). Under argon atmosphere, a sealable reaction tube (10 mL, 1.3 × 9 cm) equipped with a stirring bar was charged with amide **3a** (0.3 mmol, 89.9 mg), *N*-benzylmaleimide (0.45 mmol, 84.2 mg), $Cp^*CoI_2(CO)$ (0.03 mmol, 14.3 mg,), $AgSbF_6$ (0.06 mmol, 20.6 mg,) and NaOAc (0.03 mmol, 2.5 mg,) in dry DCE (2 mL). The tube was sealed and the mixture was heated at 120 °C for 24 h. The mixture was cooled down to room temperature and filtered through silica gel and the filtrate was concentrated under vacuum. The residue was purified by column chromatography (silica gel, petroleum ether/AcOEt 7/3 to 6/4) to obtain **9a** as white solid (104.9 mg, 72 %): mp (CH_2Cl_2): 184-187 ºC; IR (ATR): 3304, 1701, 1664 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 10.42 (s, 1H, NH), 8.73 (d, *J* = 4.9 Hz, 2H, H4', H6´), 7.71 (s, 1H, H5), 7.67 – 7.52 (m, 2H, H2'', H6''), 7.39 – 7.22 (m, 6H, H5´, H3'', H5'', 3 x Ph), 7.16 (t, *J* = 8.9 Hz, 2H, 2 x Ph), 4.68 – 4.43 (m, 3H, NCH_2, $COC\underline{H}CH_aH_bCO$), 3.20 (dd, *J* = 17.9, 9.6 Hz, 1H, $COCHC\underline{H}_aH_bCO$), 2.93 (dd, *J* = 17.9, 5.5 Hz, 1H, $COCHCH_a\underline{H}_bCO$) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, DMSO-d_6) δ 177.3, 176.3 ($\underline{C}ON\underline{C}O$), 164.1 (CO), 160.3 (C2'), 158.7 (*J* = 243.2 Hz, H4''), 157.9 (C4´,C6´), 141.1, 138.4, 138.2 (C2, C3, C4), 136.5 (Ph_C), 136.1 (d, *J* = 2.7 Hz, H1''), 128.8 (2 x Ph_H), 128.5 (C5), 127.9 (2 x Ph_H), 127.8 (Ph_H), 122.1 (*J* = 7.8 Hz, H2'', H6''), 120.1 (C5'), 115.6 (d, *J* = 22.1 Hz, H3'', H5''), 42.2 (NCH_2), 41.3 ($CO\underline{C}HCH_2CO$), 36.9 ($COCH\underline{C}H_2CO$) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.05 ppm; MS (ESI): *m/z* (rel intensity): 487 (MH^+, 100), 378 (4), 377 (15), 376 (88), 299 (8), 195 (10), 171 (6); HRMS (ESI-TOF): calcd for $C_{26}H_{20}FN_4O_3S$ [MH^+]: 487.1235; found, 487.1248.

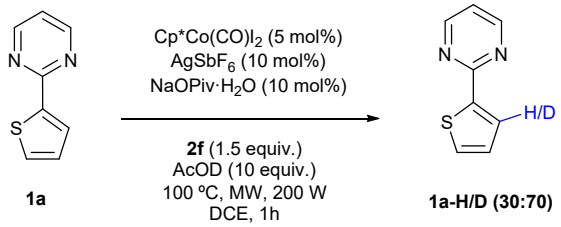


Ehyl (*E*)-3-{4-[(4-fluorophenyl)carbamoyl]-5-(pyrimidin-2-yl)thiophen-3-yl}acrylate (10a).



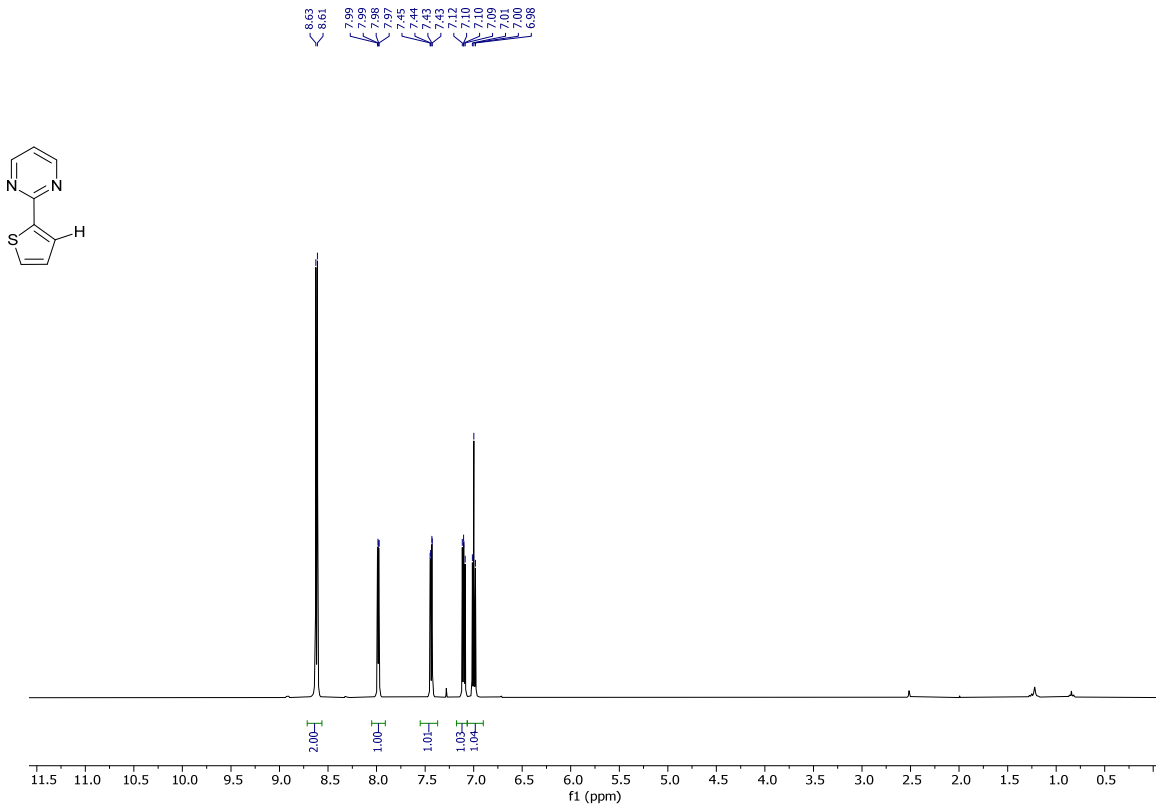
Under argon atmosphere, a sealable reaction tube (10 mL, 1.3 × 9 cm) equipped with a stirring bar was charged with amide **3a** (0.33 mmol, 100 mg), $AgSbF_6$ (0.07 mmol, 23.0 mg,) $Cp^*CoI_2(CO)$ (0.03 mmol, 15.7 mg), AgOAc (0.33 mmol, 137.0 mg) and ethyl acrylate (0.5 mmol, 53 µL) in DCE (3 mL). The tube was sealed, and the mixture was heated at 70 °C for 24 h. The mixture was cooled down to room temperature and filtered through silica gel and the filtrate was concentrated under vacuum. The residue was purified by column chromatography (silica gel, petroleum ether/AcOEt 7/3) affording **10a** as white solid (32.7 mg, 23%): mp (CH_2Cl_2): 143-145 ºC; IR (ATR): 3293, 1700, 1665 cm^{-1}; ^1H NMR (300 MHz,$CDCl_3$) δ 9.22 (s, 1H, NH), 8.68 (d, *J* = 4.9 Hz, 2H, H4´,H6´), 7.71 (d, *J* = 16.1 Hz, 1H, C<u>H</u>=CHCO$_2$Et), 7.68 – 7.55 (m, 3H, H5, H2'', H6''), 7.16 (t, *J* = 4.9 Hz, 1H, H5´), 7.10 – 7.00 (m, 2H, H3'', H5''), 6.30 (d, *J* = 16.1 Hz, 1H, CH=C<u>H</u>CO$_2$Et), 4.18 (q, *J* = 7.1 Hz, 2H, C<u>H</u>$_2$CH$_3$), 1.30 (t, *J* = 7.1 Hz, 3H, CH$_2$C<u>H</u>$_3$) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 166.6 (<u>C</u>O$_2$Et)), 163.3 (CO), 160.3 (C2'), 159.6 (d, *J* = 243.8 Hz, C4''), 157.2 (C4´,C6´), 141.4, 138.5, 137.2 (C2, C3, C4), 136.8 (<u>C</u>H=CHCO$_2$Et), 134.1 (d, *J* = 2.8 Hz, H1''), 128.8 (CH=<u>C</u>HCO$_2$Et), 122.2 (d, *J* = 8.1 Hz, H2'', H6''), 120.0 (C5), 119.3 (C5´), 115.7 (d, *J* = 22.6 Hz, C3'', C5''), 60.6 (<u>C</u>H$_2$CH$_3$), 14.3 (CH$_2$<u>C</u>H$_3$) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.60 ppm; MS (ESI): *m/z* (rel intensity): 398 (MH^+, 100), 288 (8), 287 (86); HRMS (ESI-TOF): calcd for $C_{20}H_{17}FN_3O_3S$ [MH^+]: 398.0969; found, 398.0980.

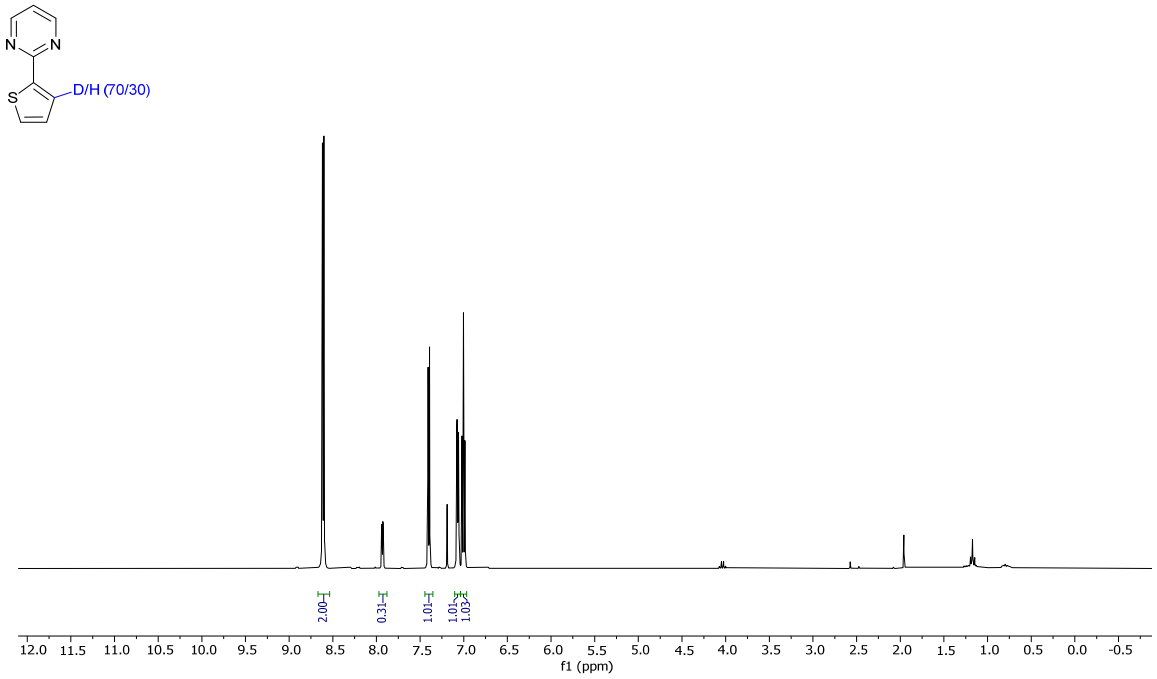
3. DEUTERIUM INCORPORATION EXPERIMENT ON 1a



1a **1a-H/D (30:70)**

Under argon atmosphere, a sealable reaction tube (10 mL, 1.3 × 9 cm) equipped with a stirring bar was charged with **1a** (0.5 mmol, 81.1 mg $Cp^*Co(CO)I_2$ (0.025 mmol, 12 mg), $AgSbF_6$ (0.05 mmol, 17.1 mg), $NaOPiv·H_2O$ (0.05 mmol, 6.2 mg), isocyanate **2f** (1 mmol, 168 mg) and AcOD (5 mmol, 0.28 mL) in DCE (2 mL). Then, the reaction tube was sealed and heated under microwave irradiation at 100 °C for 1 h, using a maximum power of 200 W. After cooling to room temperature, the mixture was filtered through silica gel and eluted with ethyl acetate. Then, the solvent was evaporated under vacuum and the residue was purified by column chromatography recovering **1a**-D/H. The deuterium incorporation was established by ^1H NMR.





^{1}H NMR spectrum of **1a** and **1a-D/H** (70/30)

4. X-RAY DIFFRACTION DATA FOR 3i

The structure of one of the thiophenecarboxamide **3i** was unambiguously confirmed by single-crystal X-ray analysis. **3i** was recrystallized from dichloromethane. **CCDC2463953** contains the supplementary crystallographic data for this structure.

A suitable crystal was selected and mounted on a SuperNova, Dual, Cu at home/near, HyPix diffractometer. The crystal was kept at 170.00(10) K during data collection. Using Olex2,[8] the structure was solved with the SHELXT[9] structure solution program using Intrinsic Phasing and refined with the SHELXL[10] refinement package using Least Squares minimization.

[8] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst*. 2009, **42**, 339-341.
[9] G. M. Sheldrick, *Acta Cryst*. 2015, **A71**, 3-8.
[10] G. M. Sheldrick, *Acta Cryst*. 2015, **C71**, 3-8.

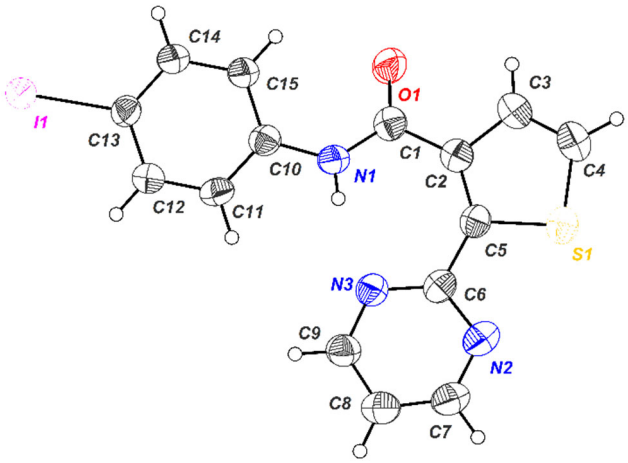


Figure S2. ORTEP plot of compound **3i** with thermal ellipsoids at the 50% probability level with the atomic nomenclature used

Crystal Data for $C_{15}H_{10}IN_3OS$ (M =407.22 g/mol): monoclinic, space group $P2_1/c$ (no.14), a = 8.55121(11) Å, b = 17.91412(18) Å, c = 10.37495(13) Å, β = 113.0049(15)°, V =1462.92(3) Å^3, Z = 4, T = 170.00(10) K, μ(Cu Kα) = 18.613 mm-1, *Dcalc* = 1.849 g/cm^3, 12871 reflections measured (9.874° ≤ 2Θ ≤ 134.15°), 2614 unique (R_{int} = 0.0972, R_{sigma} = 0.0560) which were used in all calculations. The final R_1 was 0.0632 (I > 2σ(I)) and wR_2 was 0.1583 (all data).

5. COMPUTATIONAL SUPPORTING INFORMATION

All structures were optimized using density functional theory (DFT) as implemented in Gaussian 16,[8] with B3LYP[9] as functional, 6-31G(d,p) as basis set for non-metallic atoms, and LANL2DZ[10] as basis set for cobalt. Final energies were obtained performing single-point calculations on the previously optimized structures at M06[11]/6-311++G(d,p) level of theory for non-metallic atoms and SDD basis set for cobalt,[12] introducing solvation factors with the IEF-PCM[13] method, and 1,2-dichloroethane as solvent. The stationary points were characterized by frequency calculations in order to verify that they have the right number of imaginary frequencies.

Cartesian coordinates of the optimized structures are shown below, as well as their single point energy and correction to Gibbs free energy (in kcal/mol).

Table S2. *Single point energy and correction to Gibbs free energy (in kcal/mol) for calculated complexes*

Complex	G_{Corr} (kcal/mol)	E_{SP} (kcal/mol)	Frecuency (cm^{-1})
1a	56.550	-512000.258	
Phenyl isocyanate	44.876	-250728.792	
AcOH	21.781	-143717.960	
3b	116.849	-762742.9632	
[Cp*Co(OAc)]$^+$	141.039	-479426.288	
A	215.352	-991458.388	
TS A-B	213.211	-991438.894	-778.94
B	215.689	-991451.199	
C	239.694	-1098455.587	
TS C-D	240.359	-1098442.863	-285.03
D	241.789	-1098459.393	
E	278.179	-1242187.066	
TS E-F	279.052	-1242186.704	-503.44
F	275.931	-1242199.509	

[8] Gaussian 16, Revision C.01, M. J. Frisch,G. W. Trucks, H. B. Schlegel, G. E.Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F.Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G.Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian, Inc.,* Wallingford CT, 2016.

[9] (a) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B* 1988, **37**, 785-789; b) A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648-5652; (c) W. Kohn, A. D. Becke and R. G. Parr *J. Phys. Chem.* 1996, **100**, 12974-12980.

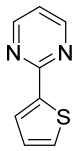
[10] T. H. Dunning Jr. and P. J. Hay, in *Modern Theoretical Chemistry* Vol. 3, (Ed. H. F. Schaefer III), Plenum, New York, 1977, pp. 1-28.

[11] Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.* 2008, **120**, 215-241.

[12] (a) M. Dolg, U. Wedig, H. Stoll and H. Preuss, *J. Chem. Phys.* 1987, **86**, 866-872; (b) D. Andrae, U. Häußermann, M. Dolg, H. Stoll and H. Preuß, *Theor. Chim.* Acta 1990, **77**, 123-141.

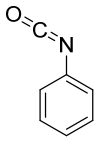
[13] a) E. Cancés, B. Mennucci and J. Tomasi, *J. Chem. Phys.* 1997, **107**, 3032-3041; b) M. Cossi, V. Barone, B. Mennucci and J. Tomasi, *Chem. Phys. Lett.* 1998, **286**, 253-260; c) J. Tomasi, B. Mennucci and E. Cancés, *Mol. Struc.: THEO CHEM* 1999, **464**, 211-226.

Cartesian Coordinates for Calculates Species



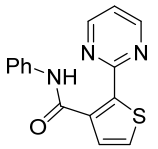
1a

C	-6.52776	1.95317	0.00000	C	-5.73344	-1.56675	0.00000
N	-6.69084	0.62936	0.00000	S	-7.32588	-2.28638	0.00000
C	-5.27024	2.55374	0.00000	C	-4.75119	-2.53181	0.00000
C	-4.17738	1.68716	0.00000	C	-6.64368	-3.87680	0.00000
C	-5.56858	-0.11668	0.00000	C	-5.27213	-3.85347	0.00000
N	-4.30755	0.36005	0.00000	H	-3.69902	-2.27665	0.00000
H	-5.14848	3.63078	0.00000	H	-7.29347	-4.74141	0.00000
H	-3.15839	2.07110	0.00000	H	-4.65834	-4.74679	0.00000
H	-7.43727	2.55154	0.00000				



C	1.46027	4.61819	3.22521	H	-0.37957	5.73820	3.13291
C	0.14106	4.83665	2.82451	H	3.14648	3.27638	3.12939
C	2.12021	3.45505	2.82266	H	1.98231	1.60911	1.71147
C	1.47186	2.51439	2.02604	H	-1.54340	4.06009	1.70892
C	-0.51864	3.90327	2.02755	N	-0.54772	1.82489	0.82673
C	0.14619	2.73870	1.62611	C	-0.39007	0.75845	0.27932
H	1.97072	5.34771	3.84606	O	-0.37219	-0.26738	-0.30076

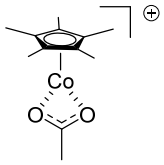
C	1.39686	-0.11139	-0.00001	H	1.68165	-0.69373	-0.88115
C	-0.09201	0.12511	0.00008	O	-0.64308	1.20264	-0.00002
H	1.68175	-0.69369	0.88112	O	-0.78040	-1.04515	-0.00001
H	1.91668	0.84545	-0.00007	H	-1.72139	-0.80020	-0.00005



3b

C	-5.56335	1.83045	-0.00515	H	-6.63593	1.86507	-0.18698
N	-5.01133	0.62257	0.03257	C	-3.12228	-0.80702	0.28858
C	-4.82399	3.00155	0.17628	S	-4.31634	-2.07016	0.02502
C	-3.46455	2.82973	0.40077	C	-1.84850	-1.35854	0.48051
C	-3.68102	0.54816	0.25661	C	-3.12239	-3.29999	0.17145
N	-2.89171	1.62240	0.44209	C	-1.88145	-2.78614	0.40779
H	-5.28156	3.98295	0.14406	H	-3.39997	-4.34102	0.07508
H	-2.80388	3.68040	0.55373	H	-0.97965	-3.36862	0.53463

C	-0.46461	-0.78799	0.74399	C	3.07657	2.95062	1.52534
O	0.47125	-1.57925	0.86668	H	3.94130	3.58259	1.70286
N	-0.33428	0.56476	0.83014	H	1.68728	4.59469	1.36490
C	0.84075	1.30363	1.06571	H	-0.27093	3.15095	0.96230
C	2.11114	0.73346	1.25623	H	2.21809	-0.34040	1.22413
C	0.70847	2.70356	1.10878	H	4.18566	1.10847	1.62859
C	1.81411	3.51612	1.33598	H	-1.19450	1.11181	0.70863
C	3.20958	1.56287	1.48298				



Co	1.06357	-1.60958	0.93150	H	3.16139	-4.42080	3.07981
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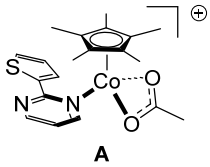
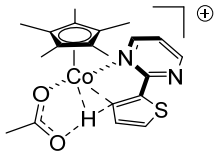
C	0.57376	-2.56002	2.73427	H	-0.22630	-4.55470	2.57184
C	1.92936	-2.81070	2.42400	H	-1.41533	-3.27128	2.32797
C	2.62945	-1.52155	2.33102	H	-0.81645	-3.62218	3.95336
C	1.69828	-0.48952	2.58548	C	-0.88158	-0.40168	3.04148
C	1.94138	0.98603	2.57100	H	-0.90161	0.58960	2.58411
H	2.91686	1.23439	2.15145	H	-0.99195	-0.26547	4.12607
H	1.90514	1.37752	3.59446	H	-1.74776	-0.96827	2.69370
H	1.17980	1.51110	1.98833	C	0.10554	-1.23291	-1.09616
C	4.07830	-1.37149	1.99658	O	0.88274	-0.38255	-0.52426
H	4.32268	-0.35733	1.67812	O	-0.14385	-2.27946	-0.38944
H	4.38621	-2.06294	1.20712	C	-0.47246	-1.01924	-2.44850
H	4.68667	-1.60220	2.88030	H	-0.53060	-1.96860	-2.98506
C	2.57564	-4.13875	2.19573	H	0.11491	-0.28641	-3.00278
H	3.26741	-4.11303	1.34892	H	-1.49430	-0.63821	-2.3333
H	1.84258	-4.92589	2.01516				



A

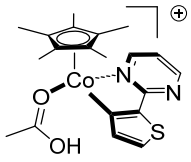
Co	1.07094	-0.27437	0.06180	H	-0.09842	-3.36705	-0.51719
C	1.77047	0.39544	-1.83407	H	0.17087	-3.59757	-2.24726
C	2.75959	-0.43566	-1.23644	C	2.83893	-2.89107	-0.33431
C	2.15396	-1.71347	-0.95625	H	2.13237	-3.52693	0.20374
C	0.82162	-1.70448	-1.51668	H	3.61695	-2.57675	0.36502
C	0.56847	-0.40436	-2.03000	H	3.31686	-3.50630	-1.10634
C	-0.64708	0.04455	-2.77853	C	4.14951	-0.04831	-0.84461
H	-1.53380	-0.52929	-2.50767	H	4.33462	-0.26613	0.21136
H	-0.47654	-0.08597	-3.85474	H	4.34459	1.01116	-1.01708
H	-0.86509	1.10120	-2.61128	H	4.87380	-0.62193	-1.43443
C	-0.12234	-2.86307	-1.48721	C	1.95197	1.80343	-2.31202
H	-1.14956	-2.55907	-1.69162	H	1.02984	2.38250	-2.22545

H	2.23932	1.80506	-3.37050	C	-4.45581	-0.28196	-0.56063
H	2.73512	2.32666	-1.75943	H	-5.45542	-0.46525	-0.93235
C	1.34385	-0.91122	2.30205	C	-2.30111	0.75640	0.10321
O	2.14825	-0.11343	1.70405	N	0.03820	1.40726	0.57801
O	0.40370	-1.37829	1.57698	S	-3.80769	1.31193	-0.60158
C	1.48018	-1.24219	3.75314	C	-1.27218	1.74555	0.38078
H	2.52664	-1.18887	4.05825	C	0.86468	2.39327	1.00151
H	1.06687	-2.23151	3.95599	H	1.88342	2.09413	1.21601
H	0.91454	-0.50868	4.33875	C	0.45382	3.70629	1.14658
H	-3.82672	-2.23553	0.14529	N	-1.70804	3.01916	0.42619
C	-3.58594	-1.18948	-0.00346	C	-0.86667	3.98099	0.78210
C	-2.35484	-0.59822	0.37872	H	1.13591	4.47480	1.48912
H	-1.55904	-1.13058	0.88019	H	-1.26004	4.99529	0.78293



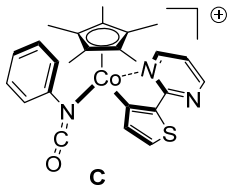
TS A-B

Co	0.62430	-0.13146	-0.09648	H	3.58928	1.40635	-0.36636
C	2.15499	0.25291	-1.47362	C	1.37438	-0.10429	2.63802
C	2.33622	-1.09268	-0.97365	O	1.72558	0.24586	1.45439
C	1.17496	-1.84041	-1.28956	O	0.29101	-0.69258	2.89445
C	0.27536	-0.97793	-2.04508	C	2.33155	0.19344	3.76669
C	0.91617	0.28305	-2.20702	H	2.80777	-0.74189	4.07876
C	0.38602	1.44344	-2.98952	H	1.77781	0.57951	4.62504
H	-0.70565	1.45596	-3.01738	H	3.10049	0.90039	3.45524
H	0.73871	1.37508	-4.02600	H	-1.30824	-3.20264	1.01843
H	0.73136	2.40104	-2.59406	C	-1.81404	-2.27621	0.77258
C	-1.00587	-1.41013	-2.68979	C	-1.16984	-0.99400	0.74374
H	-1.65808	-0.56200	-2.90778	H	-0.36017	-0.82430	1.71933
H	-1.56070	-2.10865	-2.06079	C	-3.16612	-2.21290	0.55168
H	-0.79387	-1.91413	-3.64083	H	-3.88189	-3.02497	0.55564
C	0.96899	-3.30072	-1.02588	C	-2.11190	0.00339	0.48083
H	-0.08628	-3.57278	-1.05614	N	-0.36638	1.54520	0.23957
H	1.37461	-3.60448	-0.05782	S	-3.72287	-0.59095	0.29102
H	1.48350	-3.88852	-1.79611	C	-1.71191	1.38781	0.38365
C	3.54137	-1.56935	-0.22977	C	0.13319	2.78816	0.31168
H	3.38472	-2.55482	0.21216	H	1.21180	2.88274	0.24924
H	3.80898	-0.87063	0.56673	C	-0.70672	3.88631	0.44805
H	4.39469	-1.64179	-0.91469	N	-2.58478	2.39504	0.46245
C	3.18208	1.33912	-1.37905	C	-2.08230	3.63108	0.48217
H	2.77481	2.31442	-1.65504	H	-0.31051	4.89288	0.50509
H	4.01870	1.13565	-2.05839	H	-2.80214	4.44434	0.53582



B

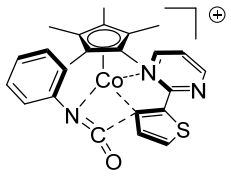
Co	0.57777	-0.16696	-0.21577	H	3.81329	0.74715	0.05988
C	2.43434	-0.00433	-1.40257	C	1.43853	0.30896	2.63488
C	2.13978	-1.37064	-0.98105	O	1.61501	0.42695	1.41074
C	0.92586	-1.77273	-1.60607	O	0.43238	-0.34837	3.16365
C	0.36365	-0.61087	-2.24152	C	2.37416	0.91440	3.63717
C	1.36344	0.44679	-2.19362	H	2.79474	0.12357	4.26565
C	1.25614	1.75357	-2.91807	H	1.81630	1.58591	4.29651
H	0.23415	2.14039	-2.92238	H	3.17143	1.45817	3.13338
H	1.54704	1.61411	-3.96655	H	-0.38389	-3.31526	1.13267
H	1.91593	2.51756	-2.50032	C	-1.11005	-2.51124	1.11948
C	-0.90034	-0.57919	-3.04656	C	-0.86027	-1.18807	0.63772
H	-1.34212	0.42011	-3.06680	H	-0.12705	-0.72510	2.44156
H	-1.64789	-1.26737	-2.64619	C	-2.39355	-2.68078	1.59351
H	-0.70268	-0.87055	-4.08570	H	-2.83044	-3.58099	2.00673
C	0.36572	-3.15788	-1.67627	C	-1.99561	-0.40240	0.78990
H	-0.72398	-3.17041	-1.62410	N	-0.69493	1.36701	0.00626
H	0.75736	-3.80366	-0.88878	S	-3.35106	-1.24666	1.48101
H	0.65805	-3.60252	-2.63603	C	-1.92693	0.99817	0.47391
C	3.07368	-2.23117	-0.18505	C	-0.47463	2.67386	-0.19447
H	2.56021	-3.08548	0.26137	H	0.51860	2.95705	-0.52446
H	3.54878	-1.66291	0.61877	C	-1.47646	3.61632	0.00801
H	3.87365	-2.62423	-0.82440	N	-2.94538	1.84068	0.66975
C	3.67586	0.74165	-1.02536	C	-2.71981	3.13316	0.42585
H	3.65243	1.77724	-1.36987	H	-1.29707	4.67146	-0.15812
H	4.55731	0.26408	-1.46840	H	-3.55997	3.80660	0.57933



C

Co	0.68944	-0.41454	0.08417	H	4.17419	0.35606	-0.72680
C	1.12319	-2.08671	1.48427	H	4.82301	-0.34755	0.75576
C	1.30736	-2.56170	0.17336	C	2.84735	-1.95944	-1.85949
C	2.27064	-1.70206	-0.49754	H	3.25193	-1.05142	-2.31135
C	2.76445	-0.76574	0.46643	H	2.10853	-2.37498	-2.54903
C	1.97822	-0.91869	1.65444	H	3.66827	-2.68423	-1.79260
C	2.16963	-0.15179	2.92748	C	0.66957	-3.76459	-0.45043
H	2.49581	0.87230	2.73323	H	0.29118	-3.55477	-1.45493
H	2.93683	-0.63172	3.54781	H	-0.15282	-4.15408	0.15302
H	1.25264	-0.10615	3.51917	H	1.41007	-4.56768	-0.54947
C	3.94450	0.14277	0.31723	C	0.30138	-2.72813	2.56345
H	3.80177	1.09332	0.83405	H	0.00912	-2.01389	3.33602

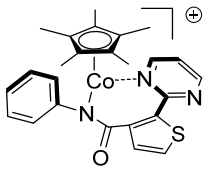
H	0.88648	-3.51032	3.06251	H	-3.15076	0.65167	3.43321
H	-0.60285	-3.20378	2.17356	H	-2.83757	3.13045	3.01817
H	2.61967	1.32966	-2.28647	C	-4.92034	-0.90582	-0.79305
C	1.96328	1.89443	-1.63511	C	-4.35981	0.20948	-1.41870
C	1.13559	1.34100	-0.61625	C	-4.09964	-1.95486	-0.37224
C	1.84435	3.26377	-1.73208	C	-2.98124	0.28370	-1.62500
H	2.36470	3.92322	-2.41499	C	-2.71994	-1.89489	-0.57443
C	0.40553	2.33040	0.01697	C	-2.17456	-0.77583	-1.20431
N	-0.64001	0.60908	1.19487	C	-0.23649	-0.50974	-2.52138
S	0.72440	3.93069	-0.59648	N	-0.73824	-0.71819	-1.40563
C	-0.56561	1.96456	1.00403	O	0.30068	-0.34933	-3.54038
C	-1.57061	0.15634	2.04671	H	-5.99300	-0.95956	-0.63783
H	-1.64824	-0.91785	2.16238	H	-4.99287	1.02657	-1.74962
C	-2.40375	1.02367	2.74291	H	-4.53305	-2.82816	0.10520
N	-1.33039	2.86038	1.63924	H	-2.53792	1.15375	-2.09984
C	-2.22969	2.38960	2.50334	H	-2.07544	-2.71181	-0.27009



TS C-D

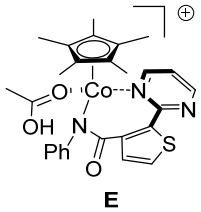
Co	-0.12784	0.61843	0.08596	H	2.47687	1.51023	2.43534
C	0.70777	2.14091	1.36163	H	-1.65037	0.60473	-3.22778
C	1.19448	2.34617	0.03930	C	-2.06566	-0.01790	-2.44458
C	0.06746	2.50565	-0.83505	C	-1.39709	-0.31411	-1.20560
C	-1.13070	2.51773	-0.02011	C	-3.24802	-0.68683	-2.59340
C	-0.74038	2.26520	1.32087	H	-3.92221	-0.66868	-3.44016
C	-1.64888	2.22940	2.51175	C	-2.17005	-1.19928	-0.44866
H	-2.66079	1.91806	2.24406	N	-0.73899	-0.82488	1.37269
H	-1.71945	3.23000	2.95574	S	-3.62828	-1.69408	-1.22713
H	-1.28178	1.55691	3.29059	C	-1.77384	-1.56945	0.89001
C	-2.51835	2.83044	-0.49046	C	-0.26748	-1.14967	2.58559
H	-3.27794	2.36985	0.14475	H	0.56800	-0.56838	2.95797
H	-2.69131	2.49548	-1.51397	C	-0.83310	-2.17471	3.33503
H	-2.67926	3.91522	-0.46203	N	-2.38795	-2.55041	1.55548
C	0.15417	2.83900	-2.29472	C	-1.92180	-2.84478	2.77046
H	-0.80987	2.73131	-2.79390	H	-0.44951	-2.42975	4.31552
H	0.88182	2.21055	-2.81546	H	-2.43256	-3.64158	3.30570
H	0.47249	3.88045	-2.42521	C	5.17359	-1.67942	-0.25577
C	2.62802	2.40376	-0.38430	C	4.59372	-1.71642	-1.52526
H	2.77230	2.00140	-1.38916	C	4.39904	-1.30870	0.84498
H	3.28350	1.85713	0.29473	C	3.25192	-1.37926	-1.70468
H	2.95688	3.45076	-0.39895	C	3.05487	-0.97533	0.67783
C	1.54545	2.05575	2.60373	C	2.47900	-1.00784	-0.59675
H	1.01105	1.58378	3.43189	C	0.36103	-1.15944	-1.65909
H	1.81745	3.06341	2.94192	N	1.09877	-0.64904	-0.73774

O	0.27100	-1.85579	-2.61650	H	4.83838	-1.28603	1.83777
H	6.21840	-1.94155	-0.12489	H	2.80759	-1.41735	-2.69334
H	5.18694	-2.00707	-2.38667	H	2.44591	-0.69997	1.53107



D

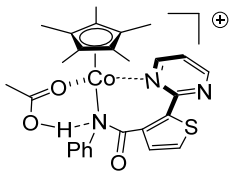
Co	-0.15389	0.32378	0.43919	C	-1.11187	0.23217	-1.82496
C	0.65144	0.90008	2.26157	C	-3.19091	1.10154	-2.45294
C	1.07347	1.87195	1.28471	H	-3.95609	1.70145	-2.92870
C	-0.09589	2.42827	0.69987	C	-1.98810	-0.60593	-1.11147
C	-1.25398	1.91652	1.42799	N	-0.67509	-1.58286	0.60438
C	-0.79859	0.98481	2.38357	S	-3.65621	-0.20524	-1.41275
C	-1.62991	0.23522	3.37943	C	-1.67176	-1.78025	-0.28586
H	-2.67122	0.15061	3.06214	C	-0.29146	-2.62211	1.36016
H	-1.61984	0.75729	4.34373	H	0.52185	-2.45358	2.05700
H	-1.24729	-0.77312	3.55632	C	-0.93397	-3.85036	1.25471
C	-2.66412	2.35085	1.18714	N	-2.37088	-2.90426	-0.41351
H	-3.38943	1.67050	1.63607	C	-2.00126	-3.93366	0.35766
H	-2.88627	2.43518	0.12028	H	-0.62958	-4.69590	1.85991
H	-2.82092	3.34293	1.62900	H	-2.57722	-4.84922	0.24995
C	-0.13357	3.49799	-0.34835	C	5.23182	-0.92124	-0.77842
H	-1.05571	3.46234	-0.93122	C	4.70885	-0.12180	-1.79709
H	0.70894	3.41620	-1.03855	C	4.36489	-1.48986	0.15699
H	-0.07852	4.48692	0.12357	C	3.33971	0.12872	-1.88213
C	2.48536	2.22714	0.95503	C	2.99316	-1.25360	0.07390
H	2.59449	2.55673	-0.07927	C	2.46126	-0.43568	-0.93795
H	3.16885	1.39287	1.11634	C	0.37221	0.01365	-2.10170
H	2.80116	3.05369	1.60493	N	1.06722	-0.20088	-0.96266
C	1.56136	0.13865	3.17407	O	0.75661	0.06779	-3.26593
H	1.06932	-0.73325	3.61190	H	6.29924	-1.10888	-0.72121
H	1.86813	0.78180	4.00906	H	5.37236	0.31409	-2.53811
H	2.46848	-0.18894	2.66212	H	4.75469	-2.12979	0.94349
H	-1.34293	1.90243	-3.25333	H	2.94067	0.72773	-2.68997
C	-1.83816	1.20600	-2.58840	H	2.31967	-1.71915	0.78489



E

Co	0.25098	-0.64423	0.40372	C	-0.90090	-0.81581	2.17661
C	0.48630	-2.52980	1.48763	C	-0.86264	-2.12984	1.56954
C	1.29996	-1.50913	2.14229	C	-2.06426	-2.90781	1.13343
C	0.44389	-0.47865	2.59294	C	-2.13765	-0.14143	2.68328

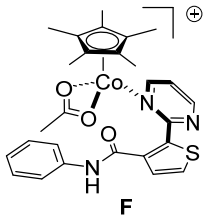
H	-2.99043	-0.27131	2.01547	C	-2.61701	-1.56391	-3.22859
H	-1.98853	0.92650	2.84115	H	-1.15969	-3.12086	-3.68413
H	-2.40604	-0.58452	3.65208	H	-3.31441	-1.79866	-4.02987
C	0.79665	0.73396	3.39840	C	4.21648	2.97481	-0.80064
H	0.46196	1.65625	2.91542	C	4.09391	2.05966	0.24591
H	1.87083	0.81595	3.56860	C	3.08091	3.32872	-1.53173
H	0.30946	0.67477	4.37880	C	2.85366	1.50278	0.56287
C	2.77227	-1.65289	2.36620	C	1.84116	2.76332	-1.22867
H	3.19650	-0.79946	2.89662	C	1.70449	1.84141	-0.16657
H	3.30841	-1.77700	1.42100	C	-0.54702	2.18236	0.38510
H	2.96539	-2.54647	2.97157	N	0.42158	1.26279	0.07169
C	1.02505	-3.81937	0.95145	O	-0.29304	3.32927	0.76427
H	0.29449	-4.34306	0.33082	H	5.18140	3.40972	-1.03987
H	1.29170	-4.49152	1.77615	H	4.96726	1.78448	0.83055
H	1.92829	-3.65193	0.35960	H	3.15526	4.04586	-2.34354
H	-2.64054	3.56940	1.40013	H	2.77328	0.80841	1.38667
C	-2.94904	2.73624	0.78283	H	0.95789	3.05913	-1.78620
C	-1.99994	1.83953	0.20838	H	4.58139	-1.79287	-1.99179
C	-4.24208	2.45408	0.43885	C	2.60978	-1.04365	-1.75252
H	-5.13894	2.97630	0.74526	C	3.56332	-2.08029	-2.27698
C	-2.61260	0.88071	-0.59354	O	1.90456	-1.24752	-0.75143
N	-0.97565	-0.89289	-1.14640	O	2.61924	0.06407	-2.45308
S	-4.35251	1.12310	-0.64465	H	2.15643	0.80495	-1.98964
C	-2.12556	-0.21349	-1.41872	H	3.33899	-3.06134	-1.86009
C	-0.65831	-1.92080	-1.96606	H	3.53069	-2.10585	-3.36860
H	0.24959	-2.45513	-1.72052	H	-1.83022	-3.62698	0.34558
C	-1.44035	-2.29412	-3.04294	H	-2.86628	-2.25536	0.78130
N	-2.94452	-0.55516	-2.43462	H	-2.45895	-3.47432	1.98605



TS E-F

Co	-0.26469	-0.82903	-0.29014	H	-1.96621	1.21723	-2.54915
C	-0.32729	-2.70410	-1.30844	H	-3.26891	0.02570	-2.42542
C	-1.57590	-2.01052	-1.55535	H	-2.27028	0.09800	-3.88584
C	-1.28509	-0.80008	-2.23895	C	-2.91582	-2.57269	-1.20046
C	0.15387	-0.71962	-2.40313	H	-3.72843	-1.88658	-1.44054
C	0.72101	-1.93599	-1.89565	H	-2.96962	-2.82127	-0.13581
C	2.16280	-2.32160	-1.99474	H	-3.08494	-3.49935	-1.76190
C	0.86978	0.29490	-3.24216	C	-0.23519	-4.07340	-0.70643
H	1.92141	0.38880	-2.96369	H	0.79476	-4.36150	-0.48650
H	0.40676	1.28017	-3.17439	H	-0.63664	-4.81881	-1.40352
H	0.83467	-0.01790	-4.29381	H	-0.82346	-4.14321	0.21374
C	-2.25614	0.19146	-2.79225	H	1.38369	4.03357	-1.50401

C	1.99915	3.32435	-0.96771	C	-2.12488	1.49420	0.45620
C	1.45898	2.12235	-0.41785	C	-0.02099	1.94758	-0.57933
C	3.33623	3.47890	-0.72541	N	-0.73209	1.08283	0.27126
H	3.97056	4.30310	-1.02406	O	-0.57757	2.63062	-1.43474
C	2.43344	1.36495	0.23045	H	-5.75304	2.66217	1.29729
N	1.47377	-0.85859	0.76704	H	-5.29605	0.28231	0.72914
S	3.98921	2.17459	0.17862	H	-3.86168	4.28484	1.35217
C	2.45758	0.07106	0.89605	H	-3.00463	-0.45254	0.22136
C	1.64865	-2.02748	1.42933	H	-1.57858	3.55173	0.83582
H	0.84402	-2.74385	1.34140	H	-2.69637	-1.04981	3.83228
C	2.76628	-2.30482	2.19213	C	-1.09194	-0.88804	2.46301
N	3.57508	-0.14674	1.62033	C	-1.71570	-1.51354	3.67762
C	3.73500	-1.29926	2.25040	O	-1.14404	-1.50547	1.35316
H	2.87570	-3.25122	2.70762	O	-0.54392	0.26080	2.60544
H	4.65631	-1.42268	2.81547	H	-0.42187	0.72940	1.57407
C	-4.74392	2.33630	1.06648	H	-1.85046	-2.58666	3.54250
C	-4.48649	1.00651	0.74670	H	-1.11018	-1.30265	4.56133
C	-3.68305	3.24545	1.09438	H	2.45774	-3.03613	-1.22390
C	-3.18596	0.58714	0.44550	H	2.82328	-1.45381	-1.93617
C	-2.38783	2.83101	0.80061	H	2.33924	-2.79880	-2.96700

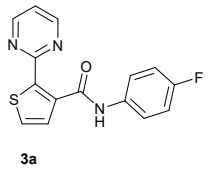


F

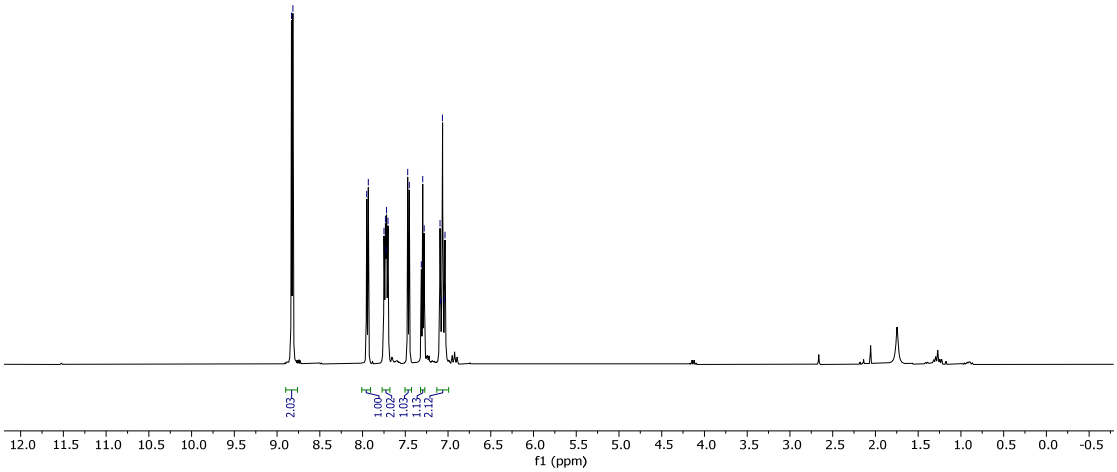
Co	-1.58846	-0.81902	-0.02239	H	-5.53487	-0.94018	-1.35572
C	-3.67181	-0.95363	-0.29678	H	-4.20599	-1.65174	-2.26845
C	-3.21264	-2.16737	0.31942	H	2.43085	2.54108	2.54576
C	-2.56262	-1.82013	1.54128	C	1.51982	2.61146	1.96286
C	-2.71512	-0.38828	1.74192	C	1.26475	1.88571	0.75231
C	-3.42276	0.13318	0.62754	C	0.51522	3.47303	2.29469
C	-3.88770	1.54021	0.42367	H	0.45540	4.13795	3.14542
C	-2.23111	0.34584	2.95276	C	0.03740	2.20647	0.20349
H	-2.28737	1.42721	2.82635	N	-1.03605	0.59570	-1.34533
H	-1.19437	0.08519	3.18383	S	-0.76189	3.44070	1.12982
H	-2.84068	0.07423	3.82305	C	-0.47717	1.81562	-1.13320
C	-1.90720	-2.74973	2.51459	C	-1.30980	0.26542	-2.62544
H	-0.97995	-2.32291	2.90404	H	-1.68514	-0.73678	-2.79084
H	-1.67200	-3.71445	2.06122	C	-1.12573	1.15353	-3.67300
H	-2.57409	-2.93747	3.36467	N	-0.35863	2.74990	-2.07905
C	-3.31376	-3.53460	-0.27619	C	-0.68532	2.43054	-3.33181
H	-2.54605	-4.20576	0.11118	H	-1.34481	0.86804	-4.69495
H	-3.22077	-3.50976	-1.36399	H	-0.58340	3.21739	-4.07562
H	-4.29208	-3.96810	-0.03459	C	6.71878	-1.61624	-0.38921
C	-4.46192	-0.85369	-1.56702	C	5.90819	-1.05225	-1.37514
H	-4.30782	0.10462	-2.06914	C	6.38706	-1.43659	0.95518

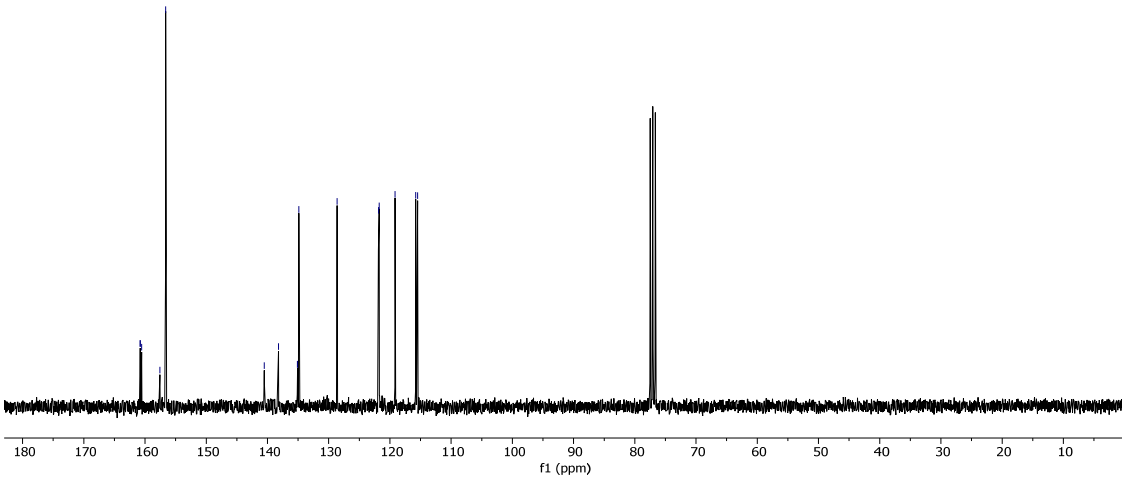
C	4.77170	-0.31431	-1.04047	H	2.21932	-2.87660	0.39496
C	5.25435	-0.70662	1.30601	C	0.42418	-1.95865	-0.30111
C	4.44004	-0.14328	0.31206	C	1.72236	-2.64822	-0.54978
C	2.22515	0.99830	0.02414	O	-0.59083	-2.12564	-1.06921
N	3.32411	0.61627	0.74379	O	0.24338	-1.14174	0.66333
O	2.02658	0.67983	-1.14981	H	3.31067	0.81788	1.73261
H	7.60114	-2.18524	-0.66380	H	1.56656	-3.55530	-1.13555
H	6.16264	-1.17820	-2.42332	H	2.36462	-1.96143	-1.11113
H	7.00966	-1.86409	1.73510	H	-3.73737	1.87625	-0.60584
H	4.15047	0.12657	-1.80726	H	-3.38701	2.24070	1.09154
H	5.00030	-0.57095	2.35513	H	-4.96442	1.59706	0.62577

6. **COPIES OF ^{1}H- AND ^{13}C{^{1}H}-NMR (AND ^{19}F-NMR) SPECTRA OF AMIDES 3a-x, 3ba, 5aa-5bk, 7a,b, 8a,b, 9a, 10a**

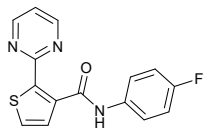


3a

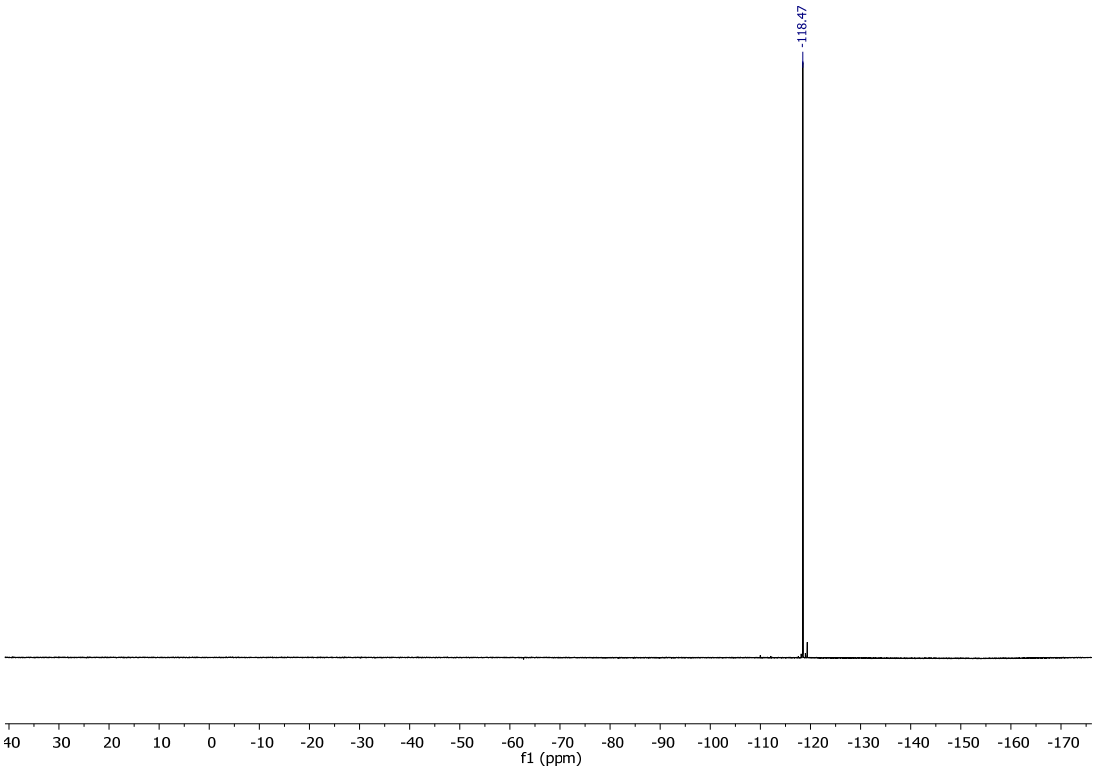




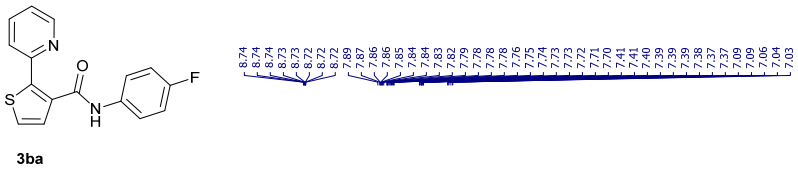
^{1}H and ^{13}C{^{1}H}-NMR spectra of **3a**



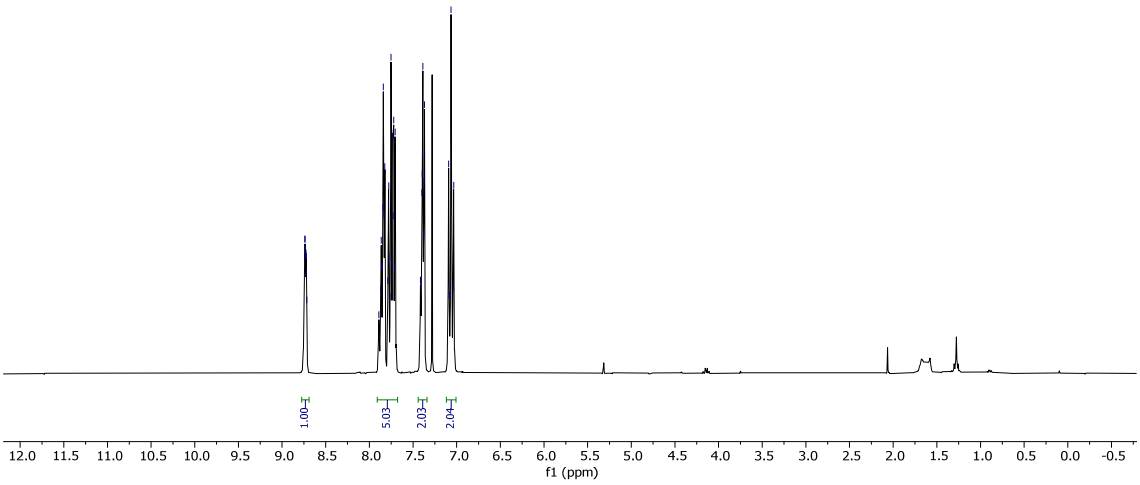
3a

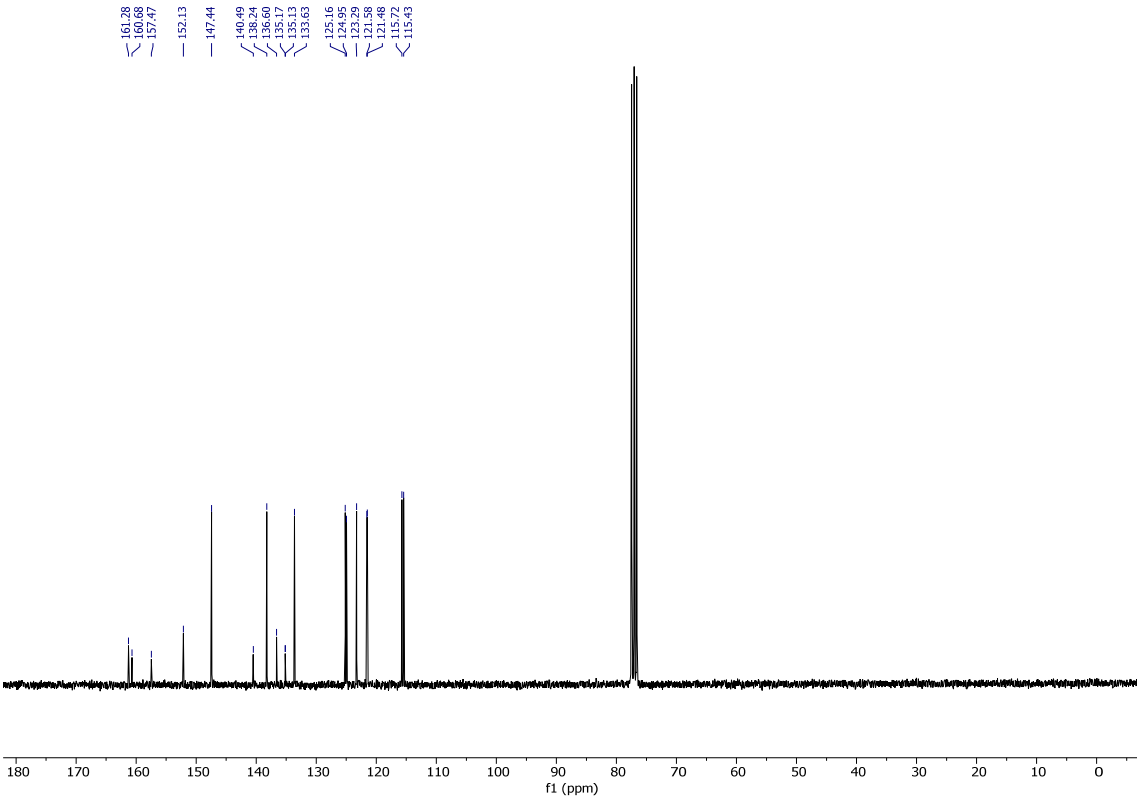


^{19}F NMR spectrum of **3a**

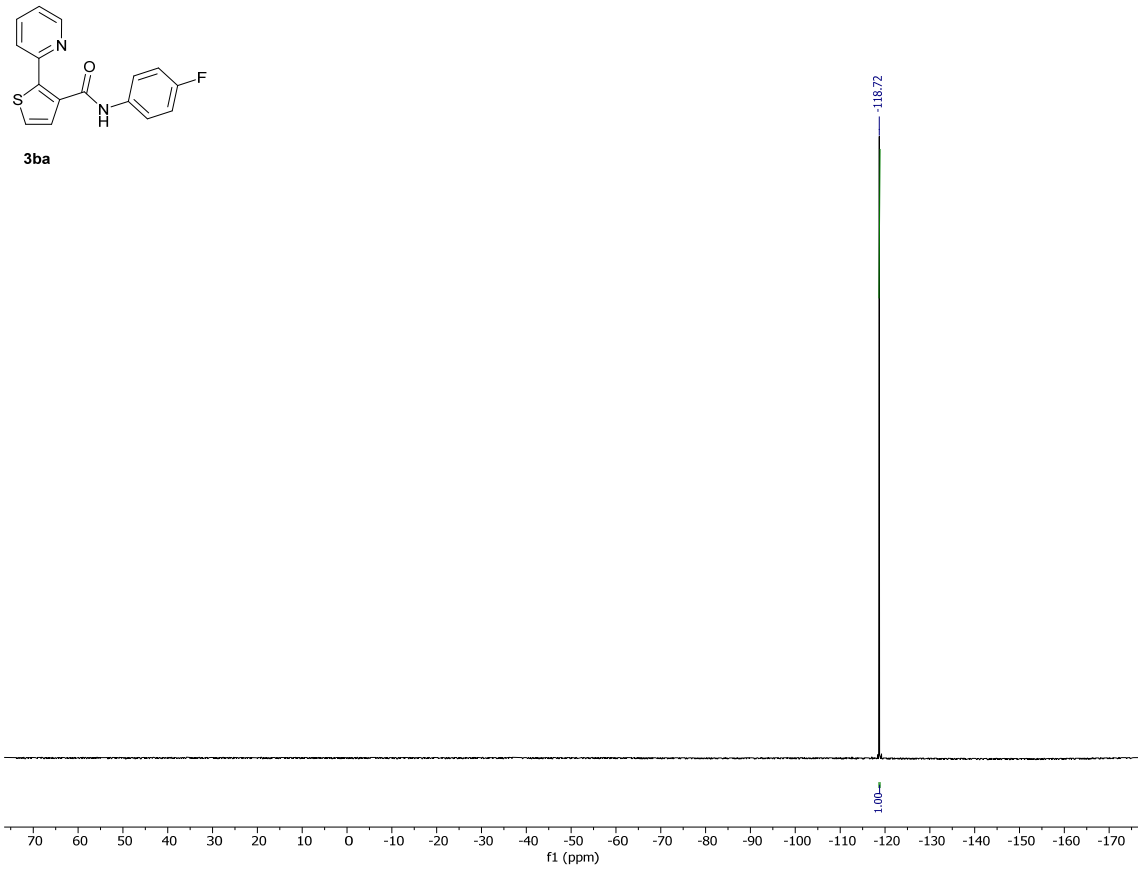


3ba

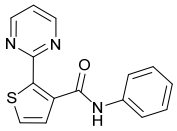




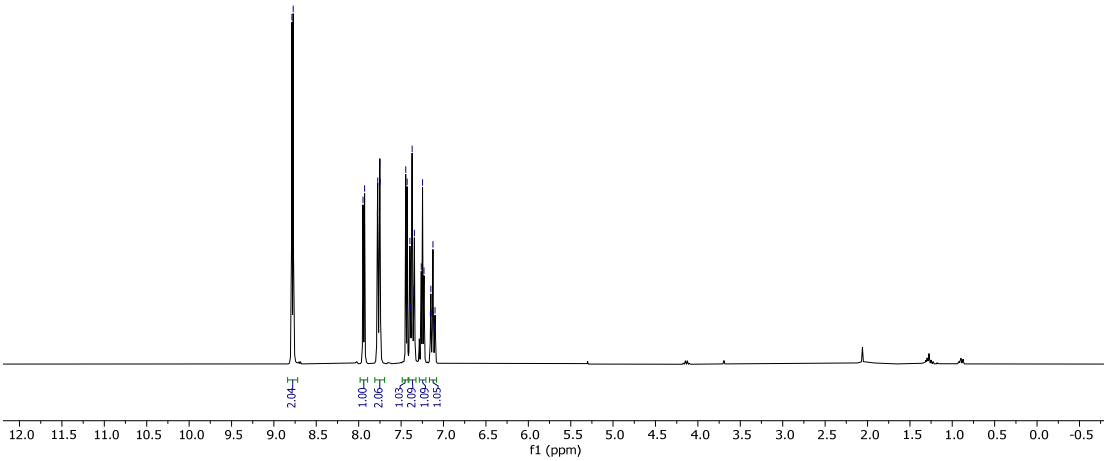
^{1}H and ^{13}C{^{1}H}-NMR spectra of **3ba**

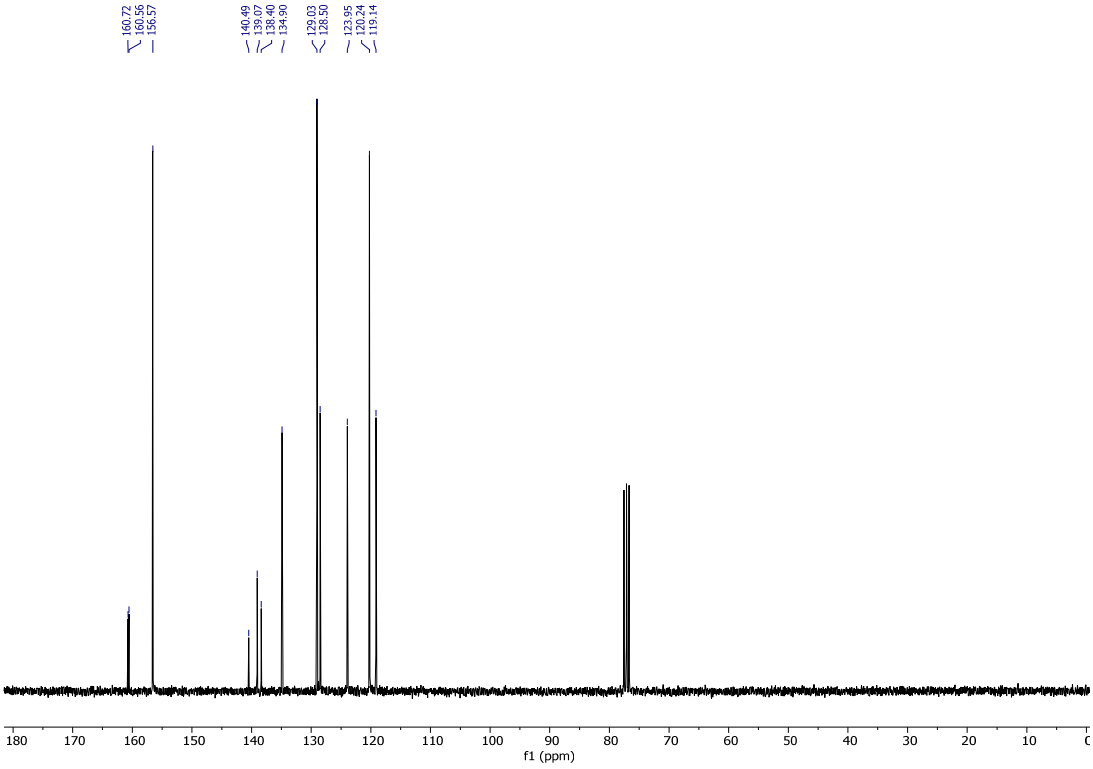


^{19}F NMR spectrum of **3ba**

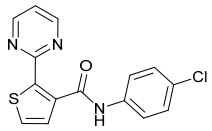


3b

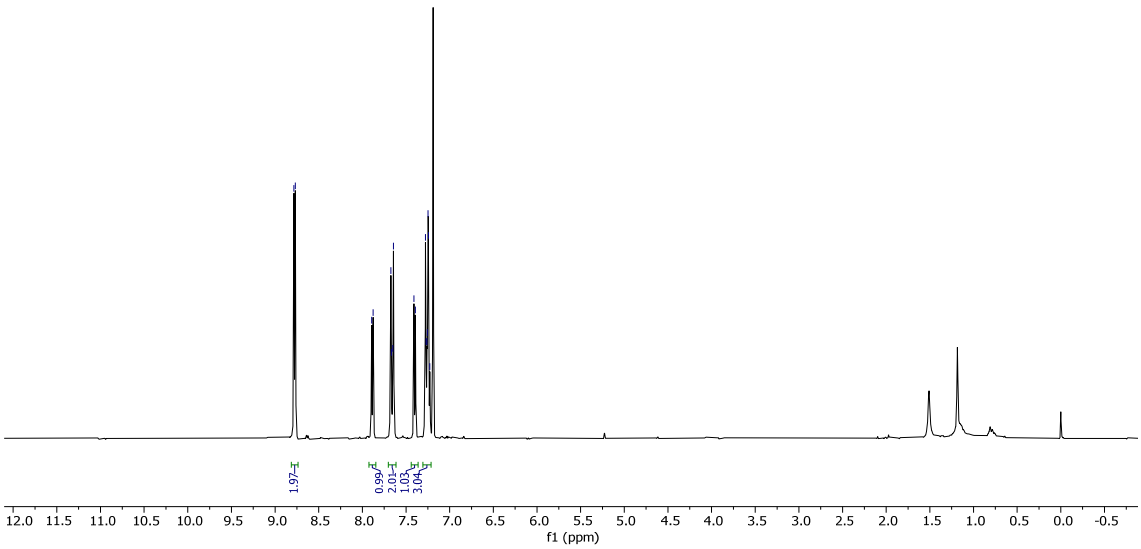




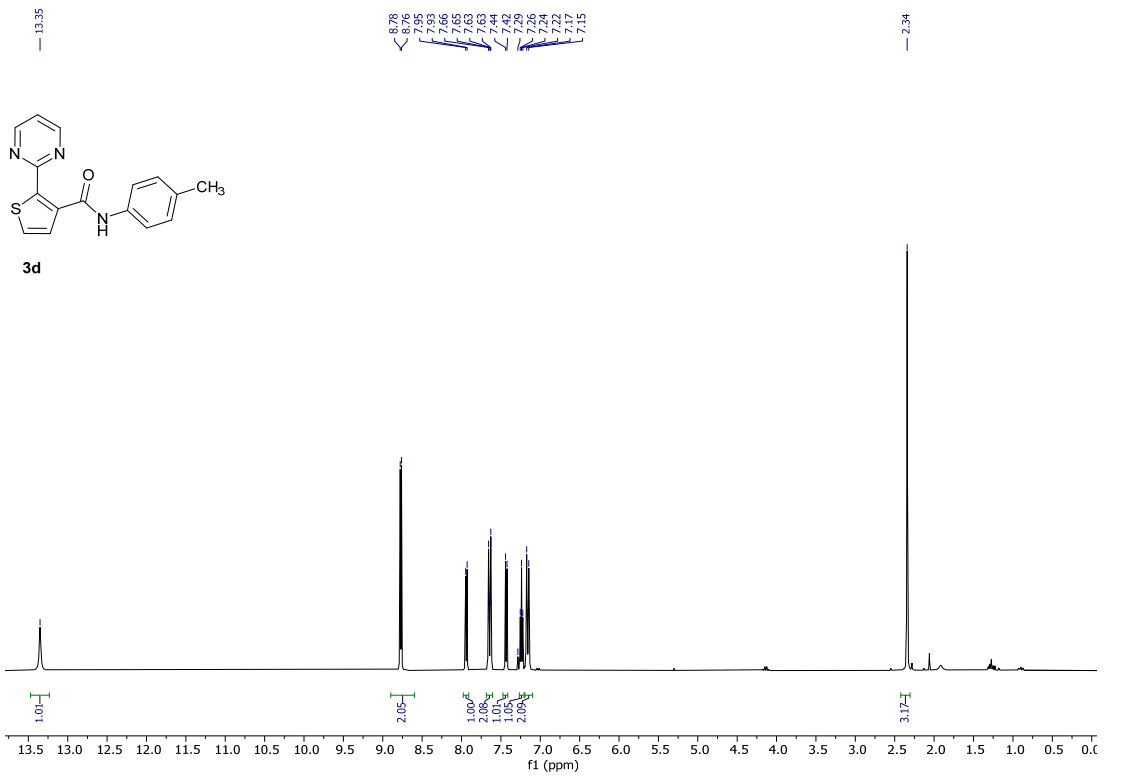
^{1}H and $^{13}C\{^{1}H\}$-NMR spectra of **3b**

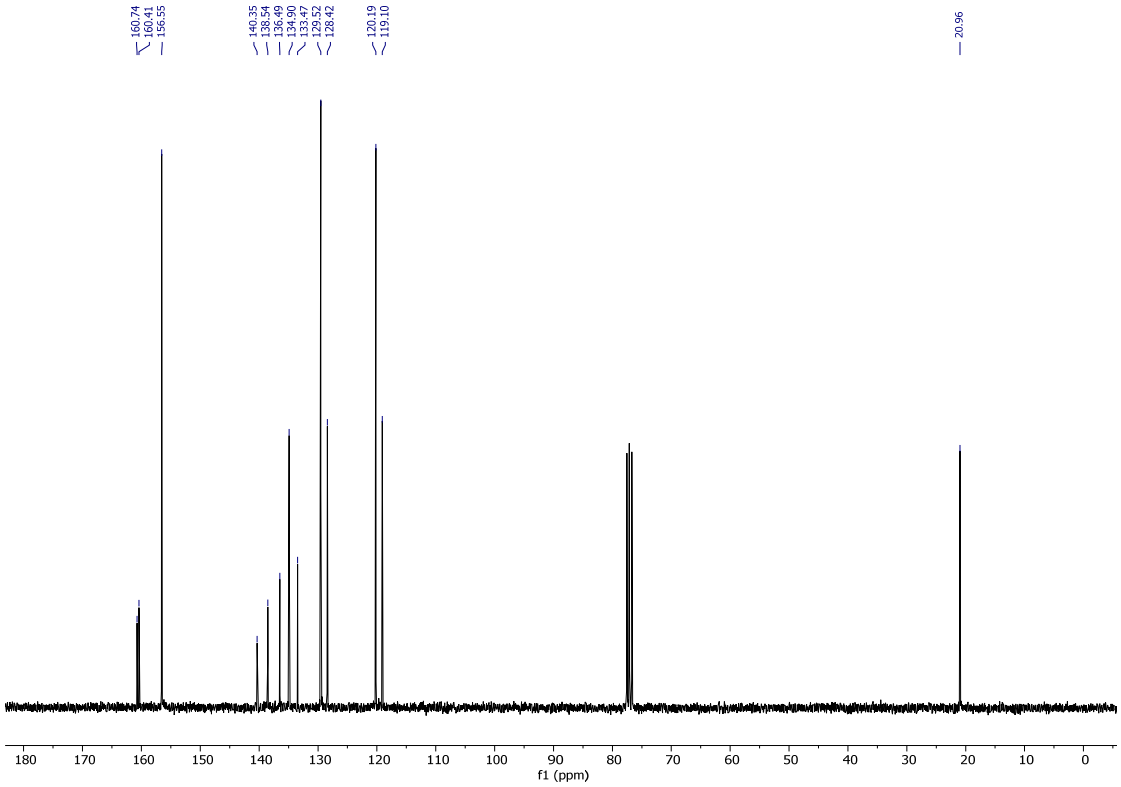


3c

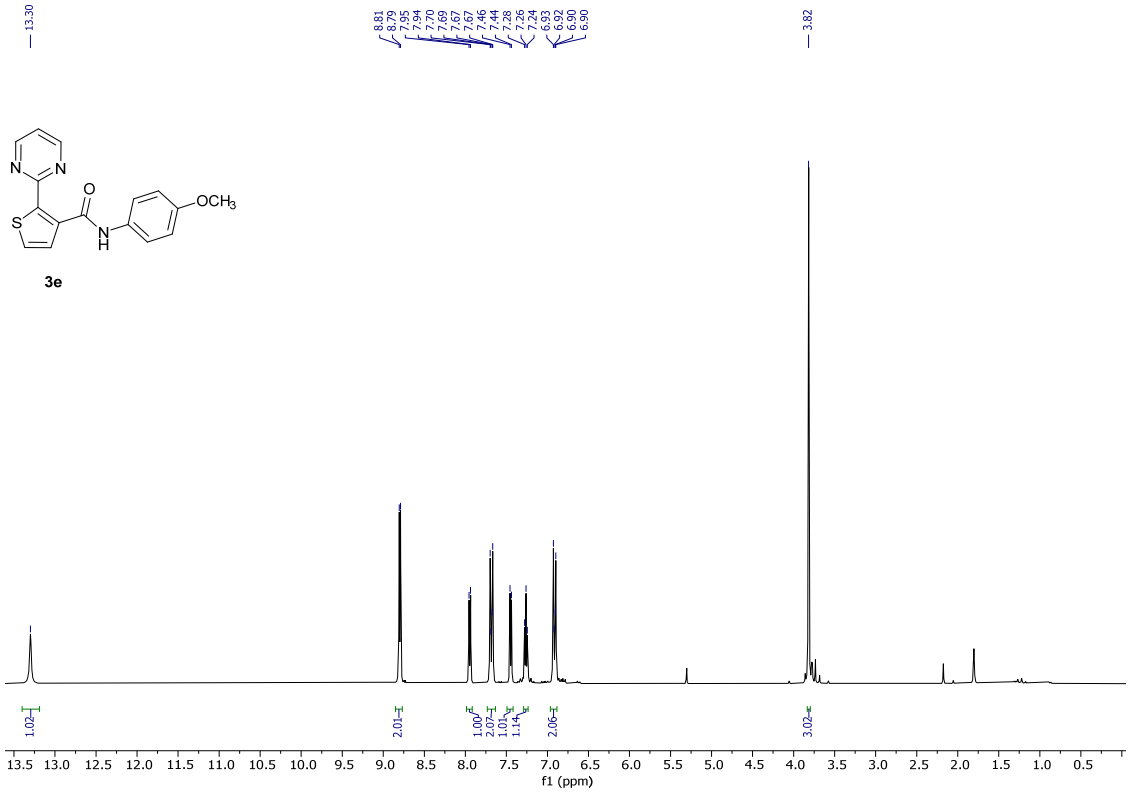


^{1}H and ^{13}C{^{1}H}-NMR spectra of **3c**

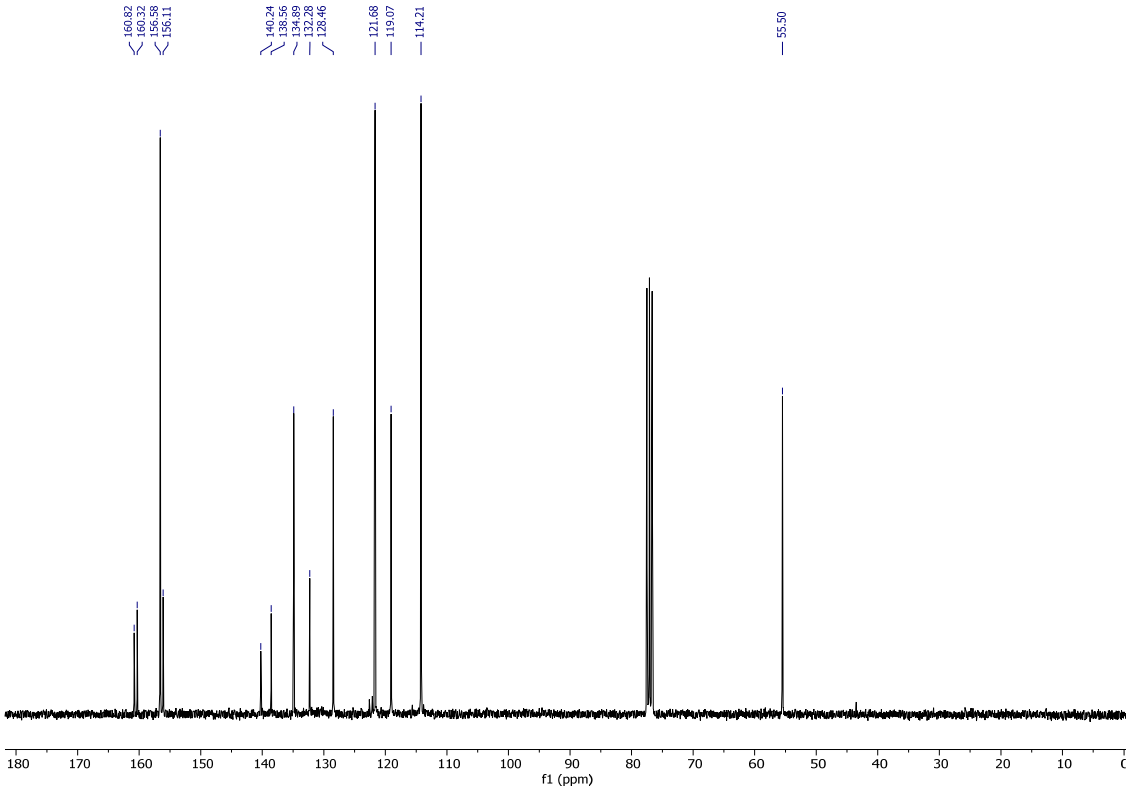




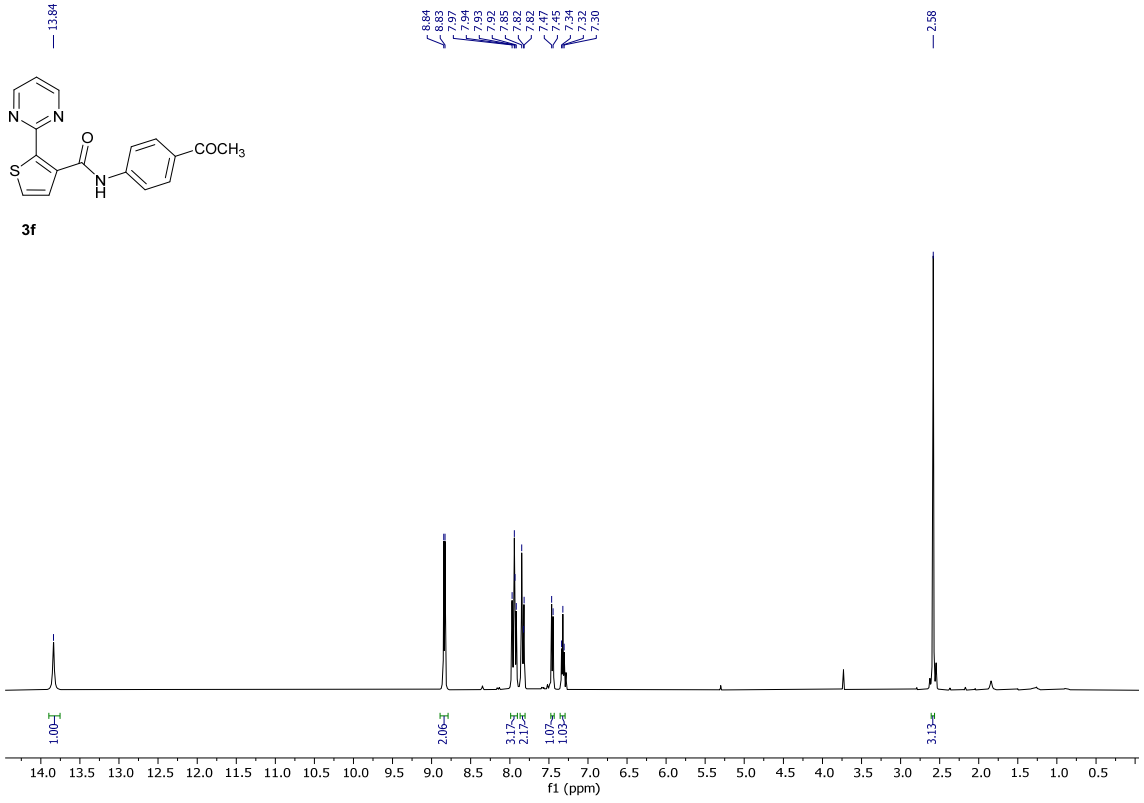
^{1}H and $^{13}C\{^{1}H\}$-NMR spectra of **3d**



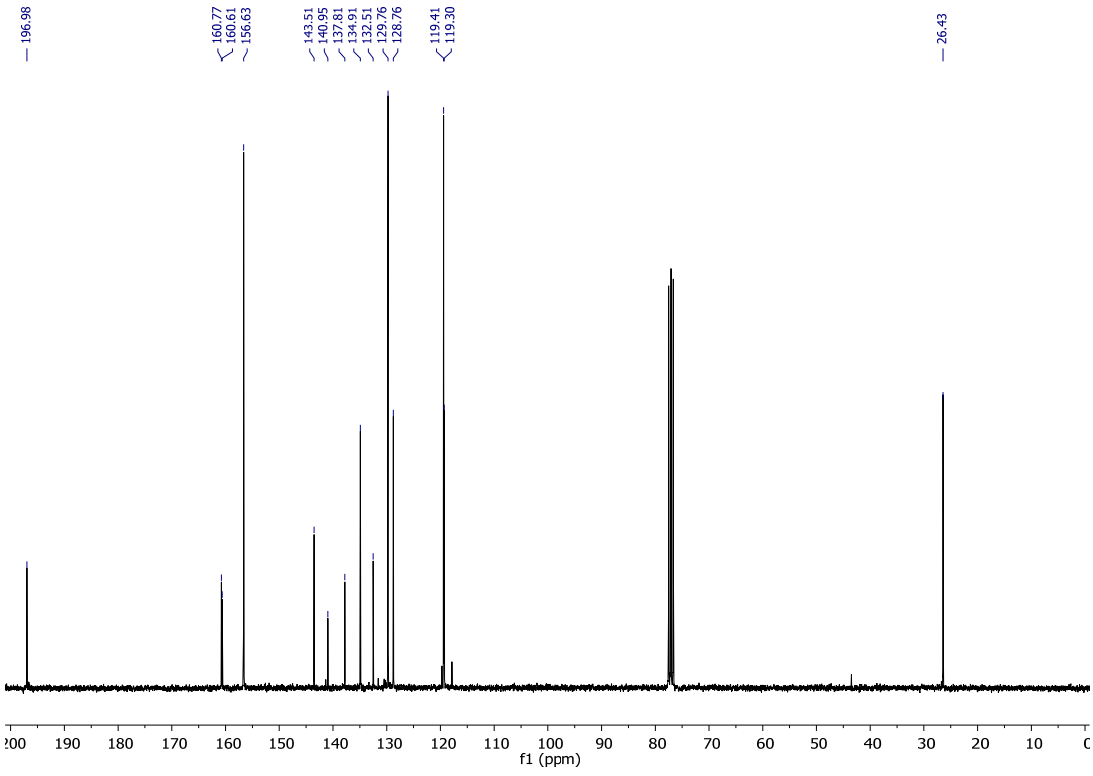
3e



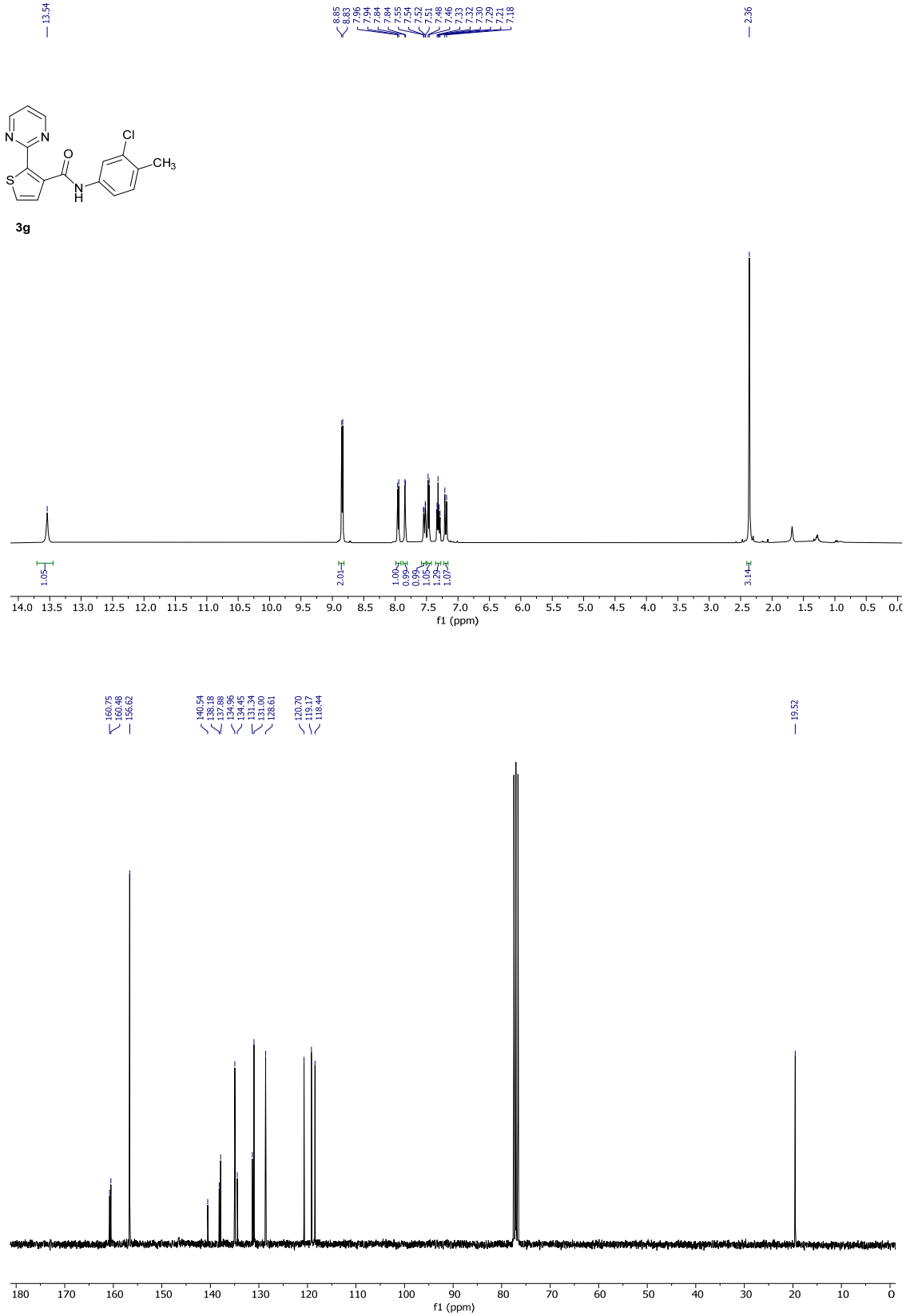
^{1}H and $^{13}C\{^{1}H\}$-NMR spectra of **3e**



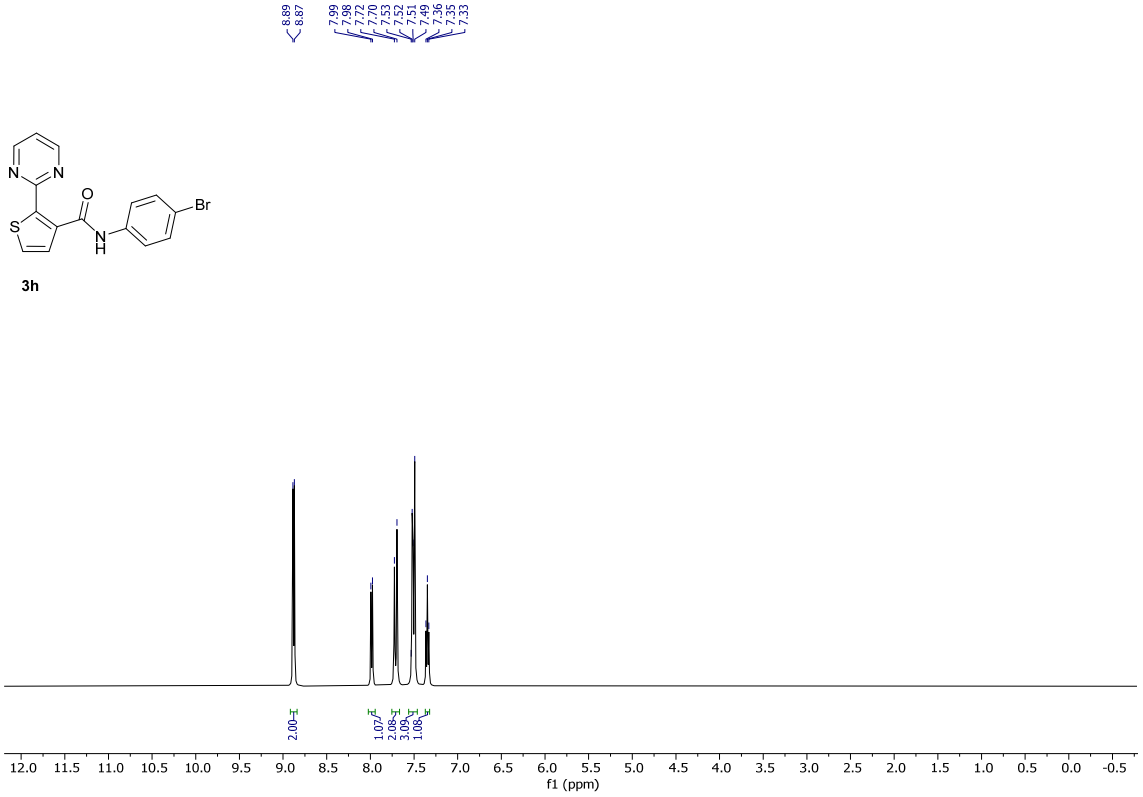
3f



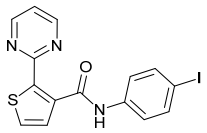
^{1}H and $^{13}C\{^{1}H\}$-NMR spectra of **3f**



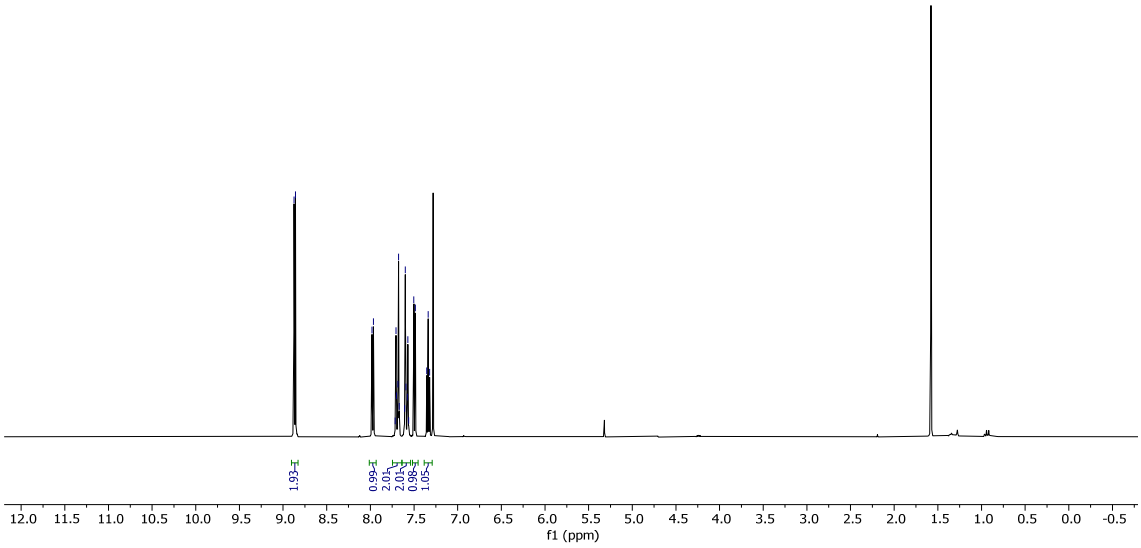
^{1}H and $^{13}C\{^{1}H\}$-NMR spectra of **3g**

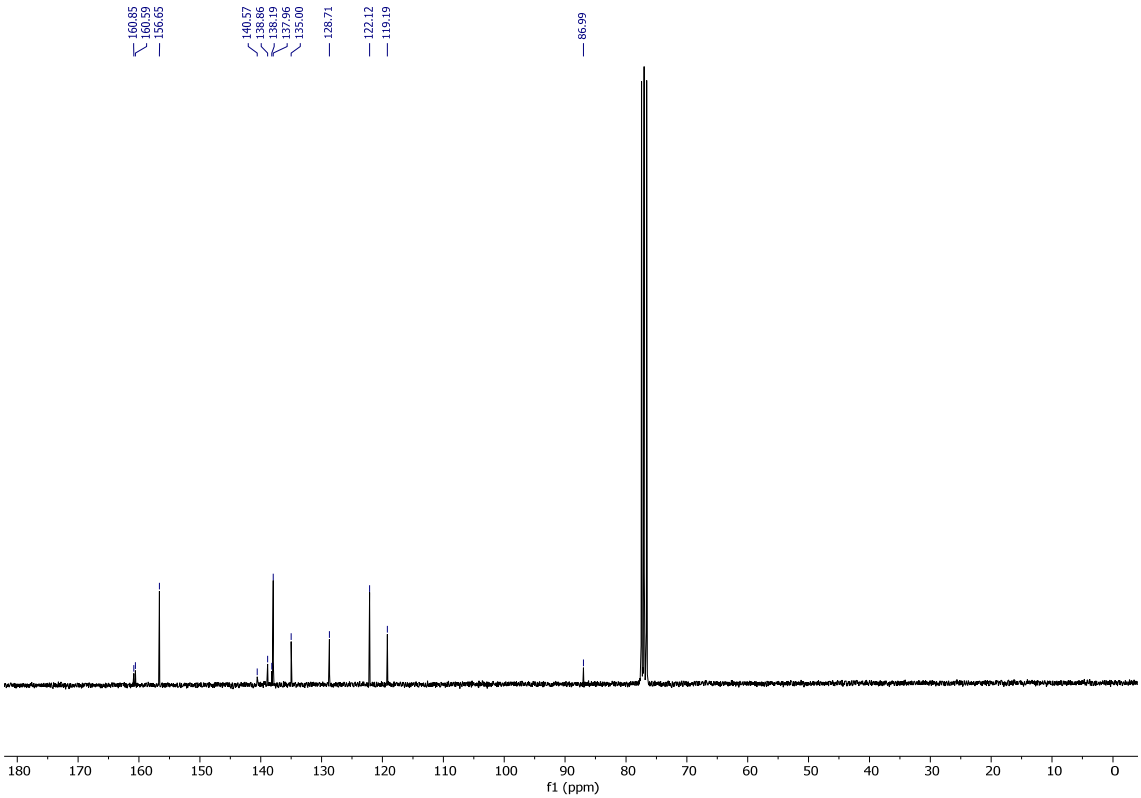


^{1}H and ^{13}C{^{1}H}-NMR spectra of **3h**

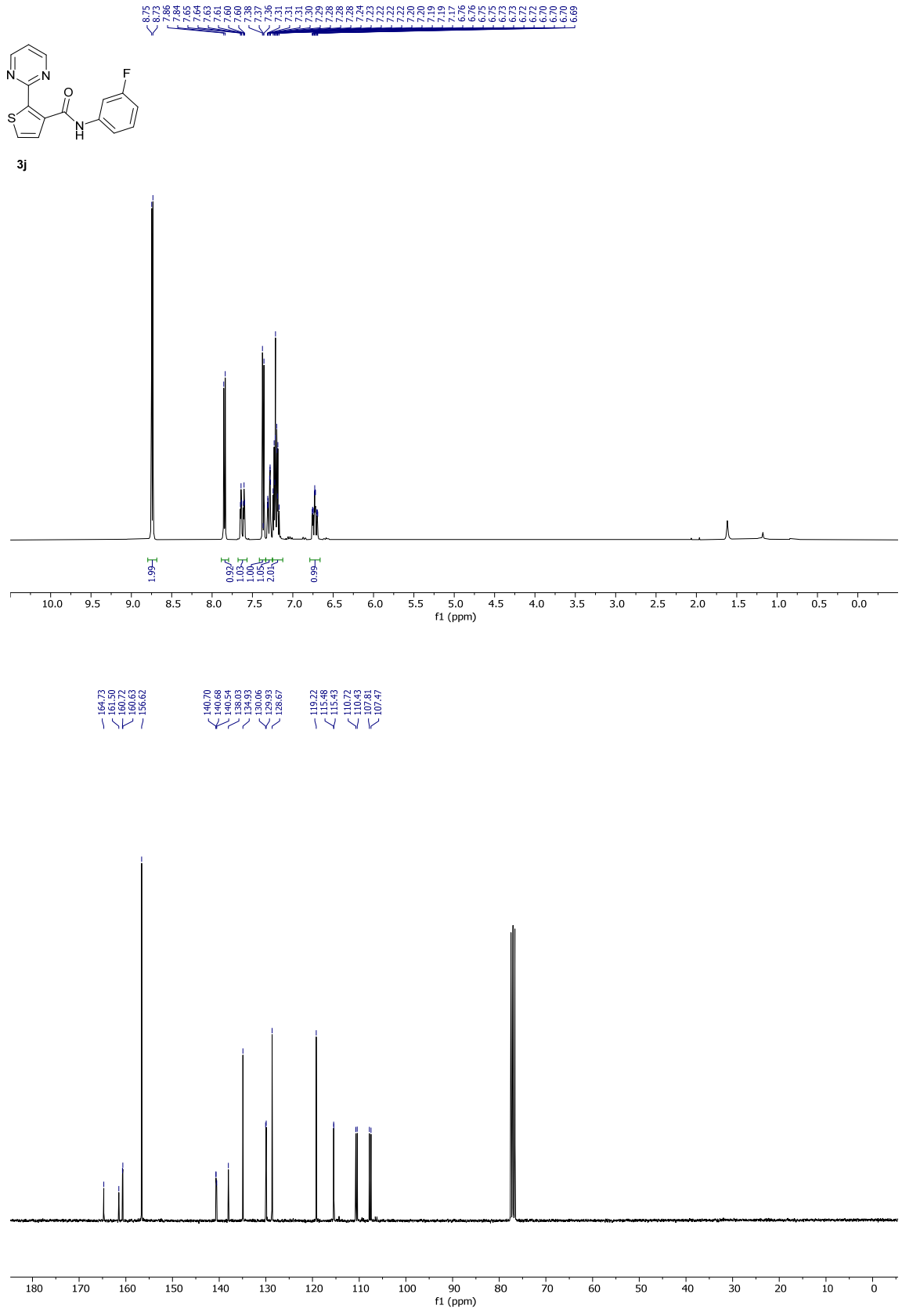


3i

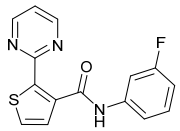




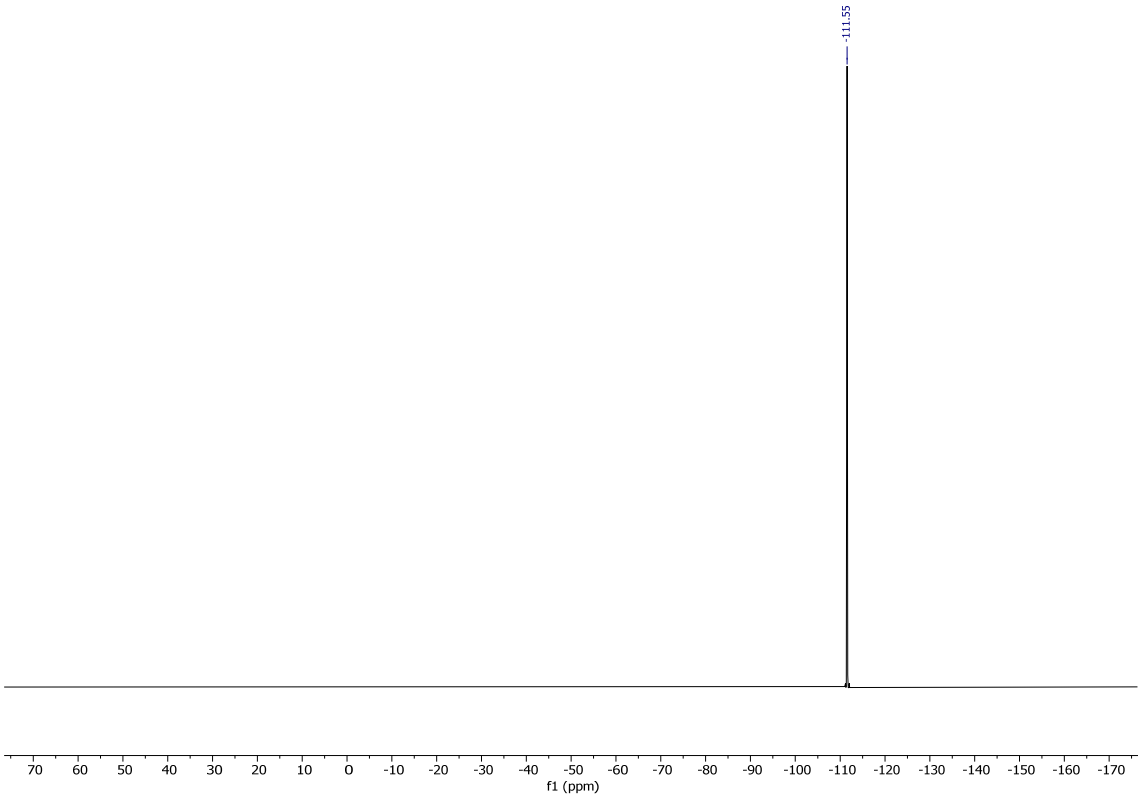
^{1}H and ^{13}C{^{1}H}-NMR spectra of **3i**



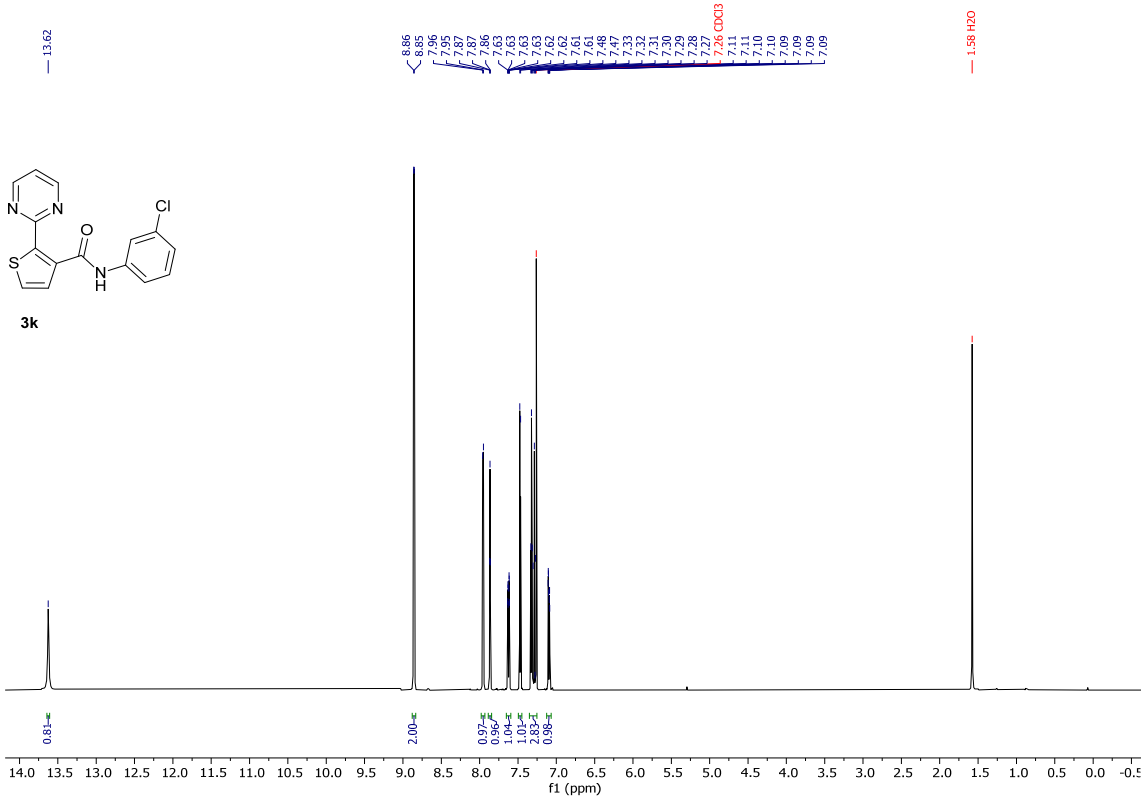
^{1}H and $^{13}C\{^{1}H\}$-NMR spectra of **3j**

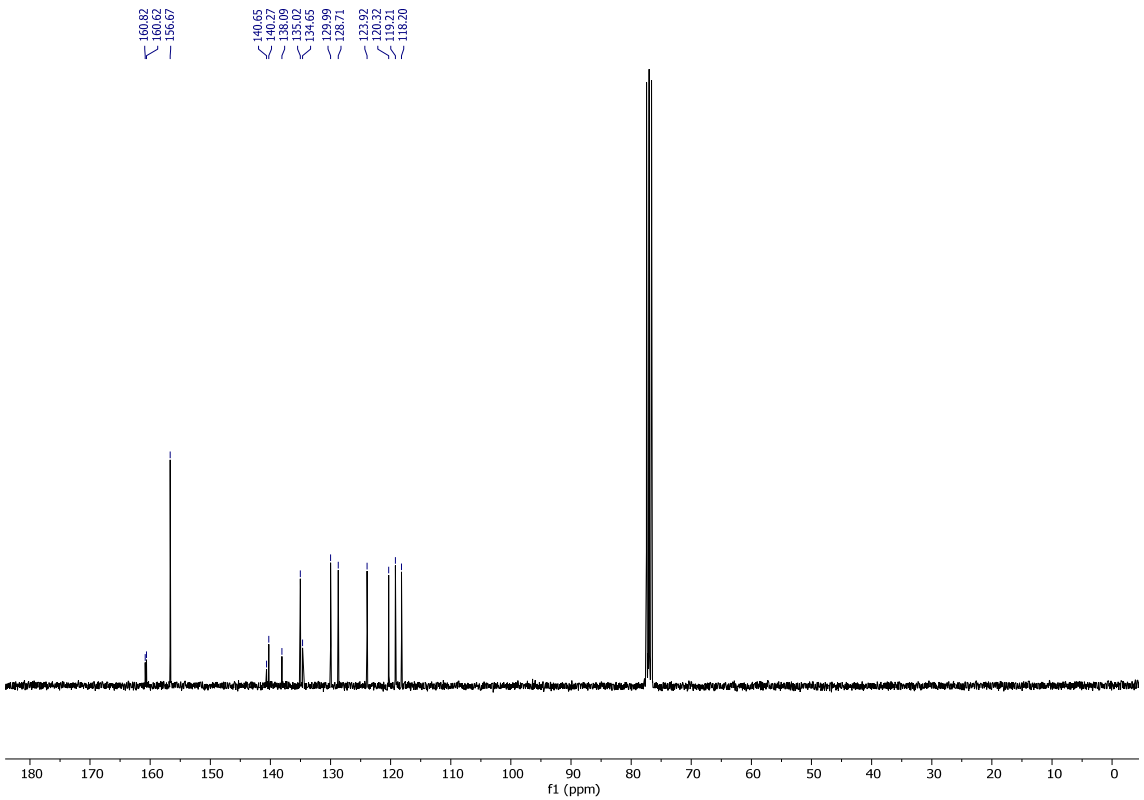


3j

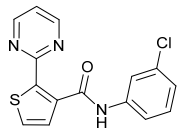


^{19}F NMR spectrum of **3j**

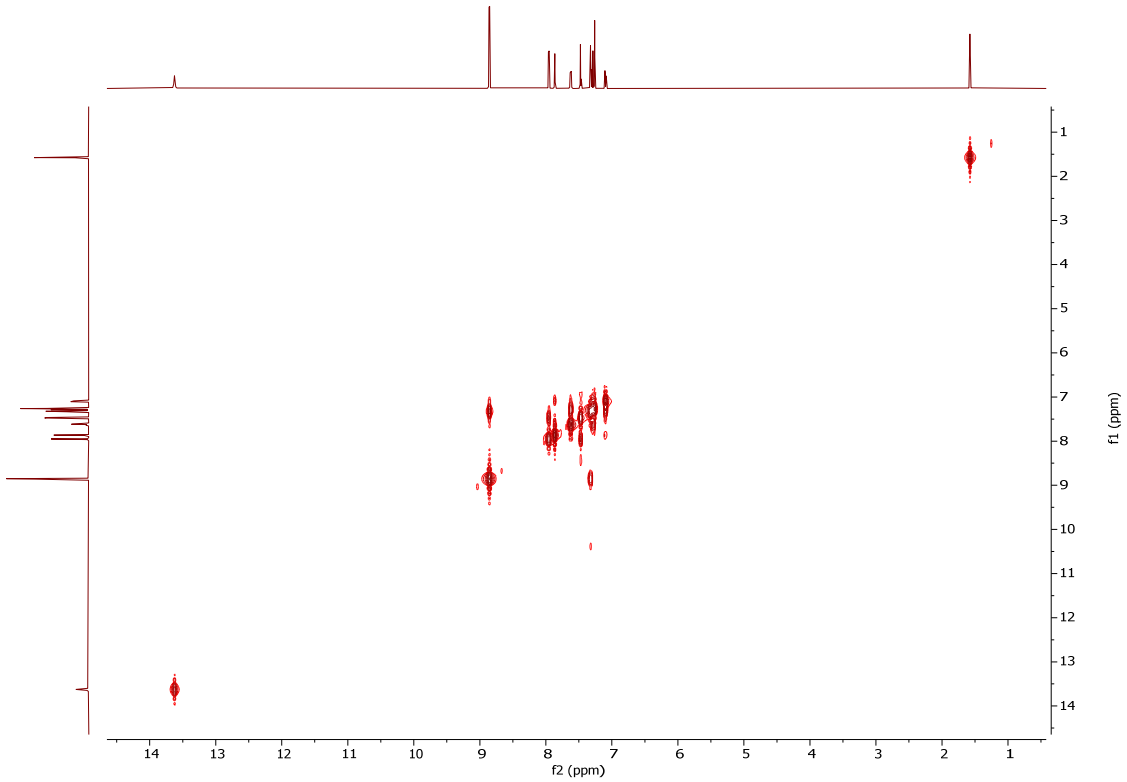




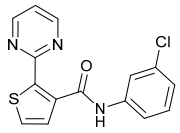
^{1}H and $^{13}C\{^{1}H\}$-NMR spectra of **3k**



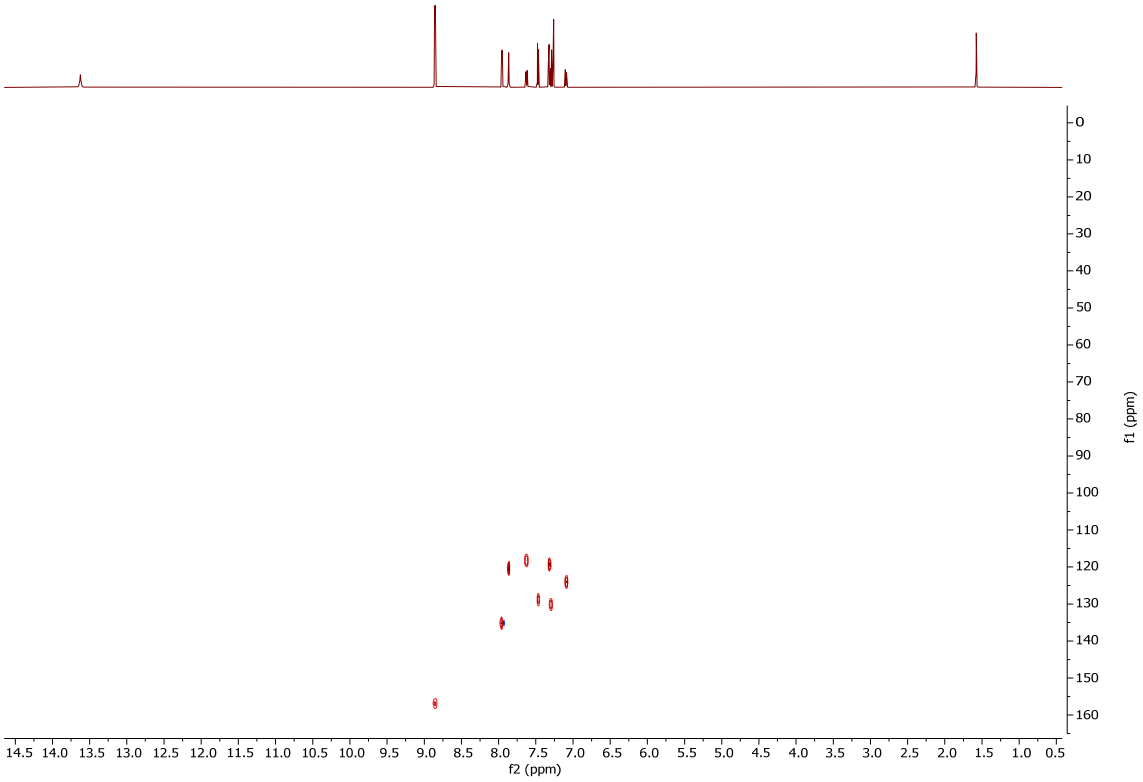
3k



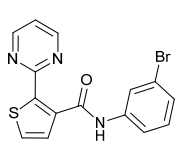
COSY spectrum of **3k**



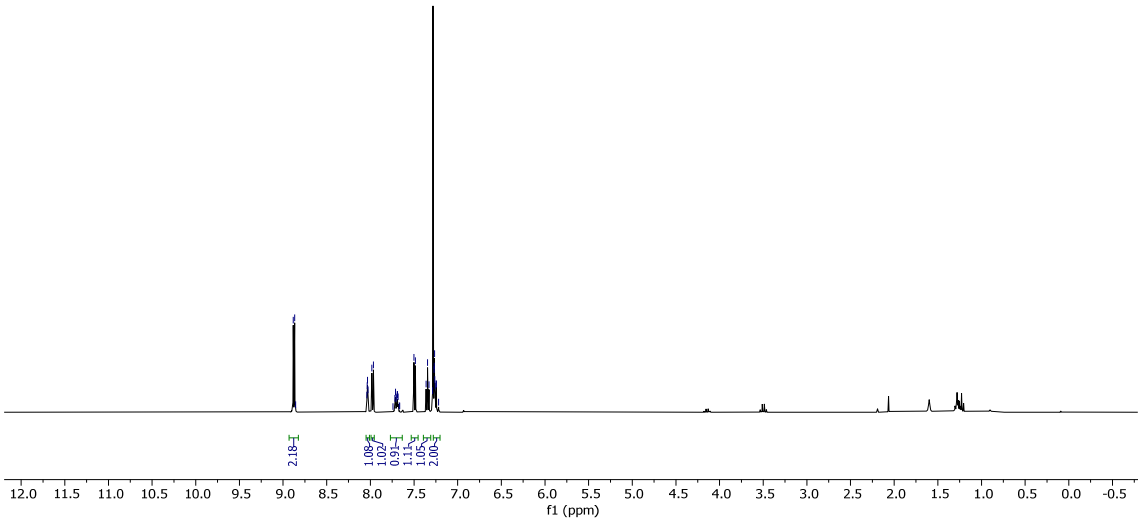
3k

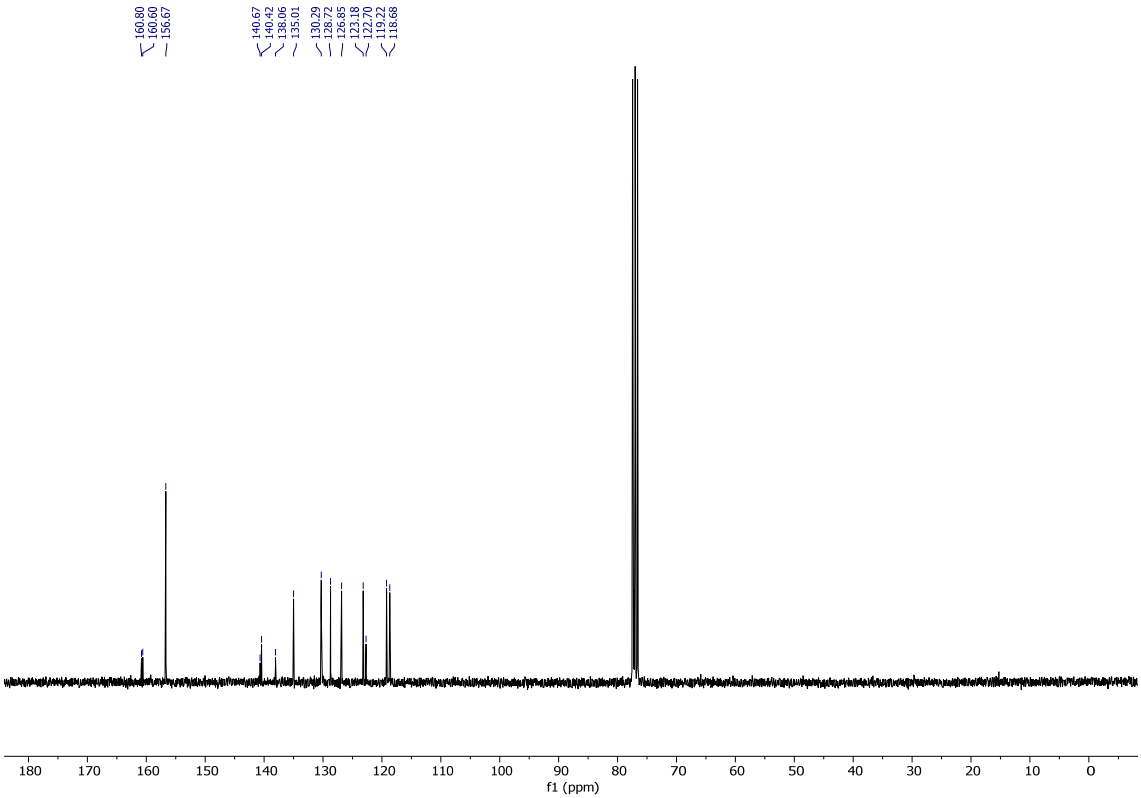


HSQC spectrum of **3k**

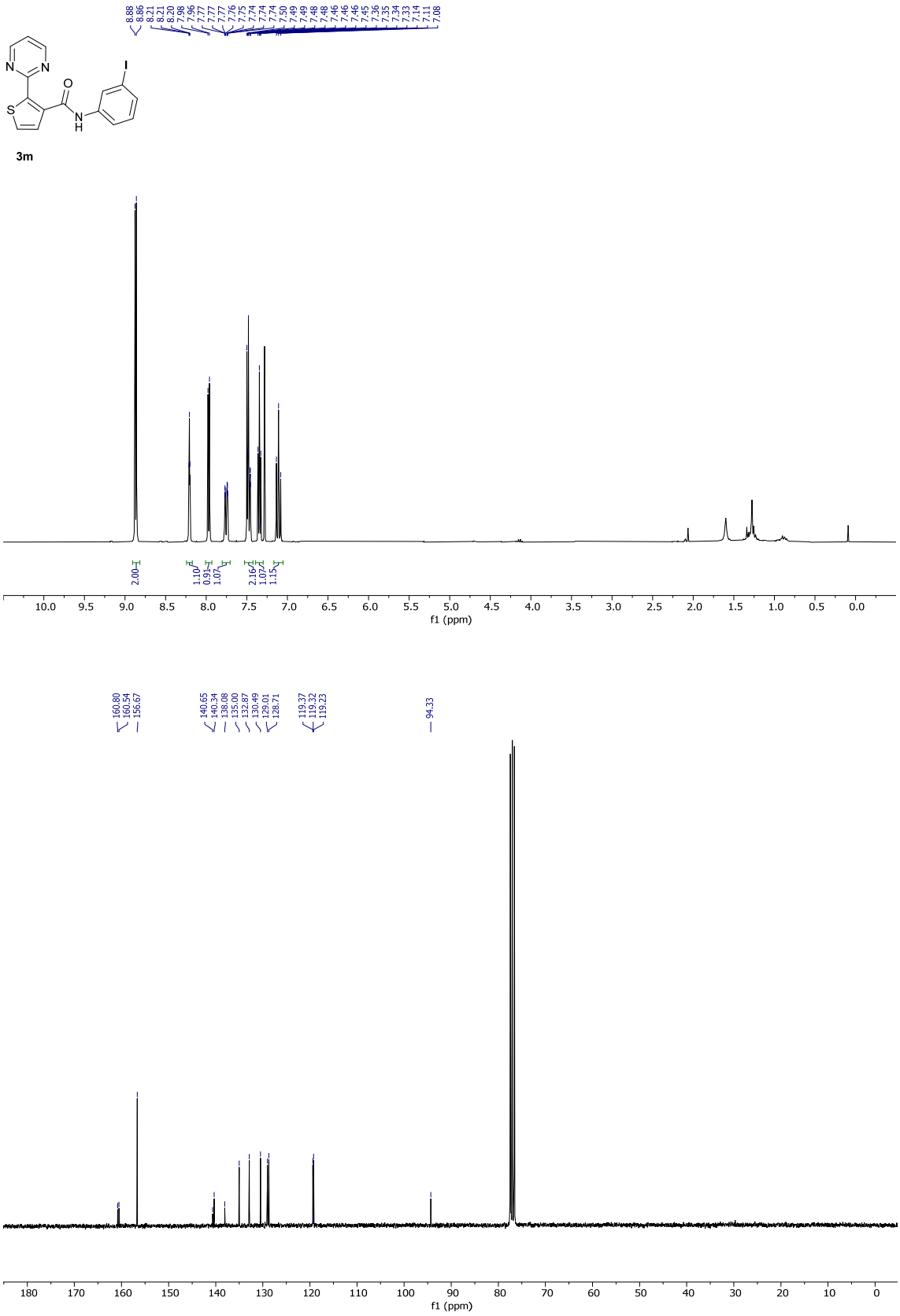


3l

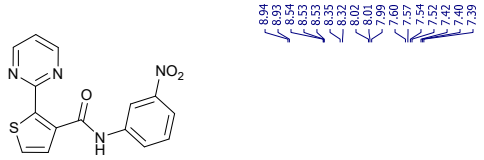




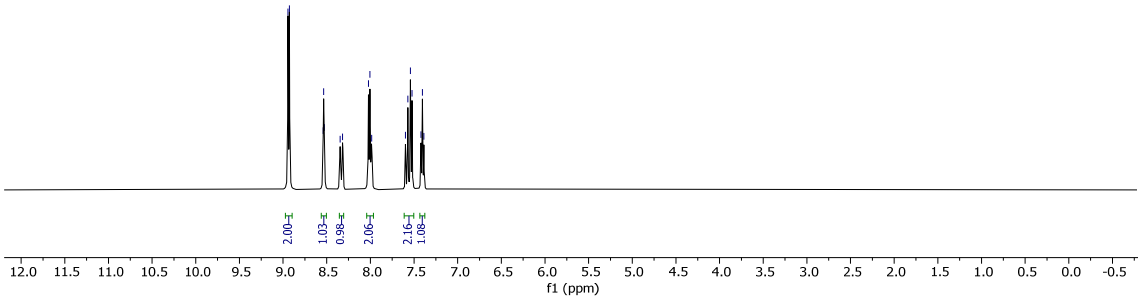
^{1}H and ^{13}C{^{1}H}-NMR spectra of **3l**

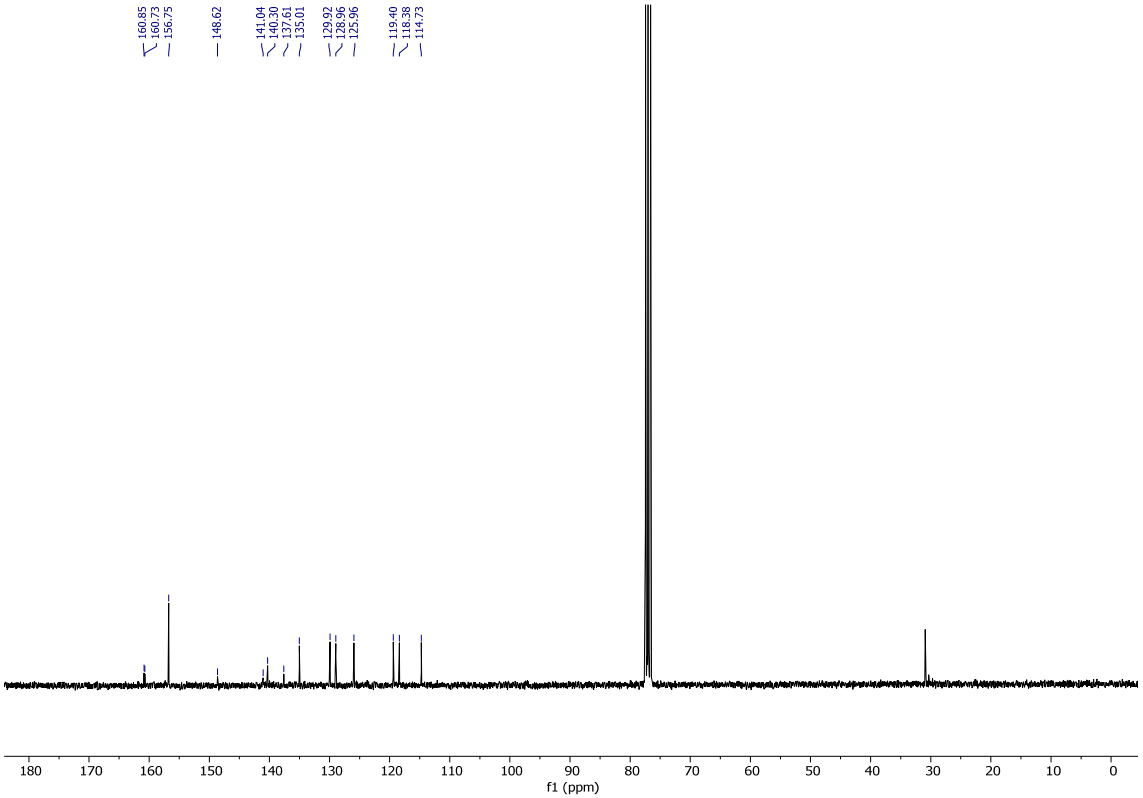


^{1}H and ^{13}C{^{1}H}-NMR spectra of **3m**

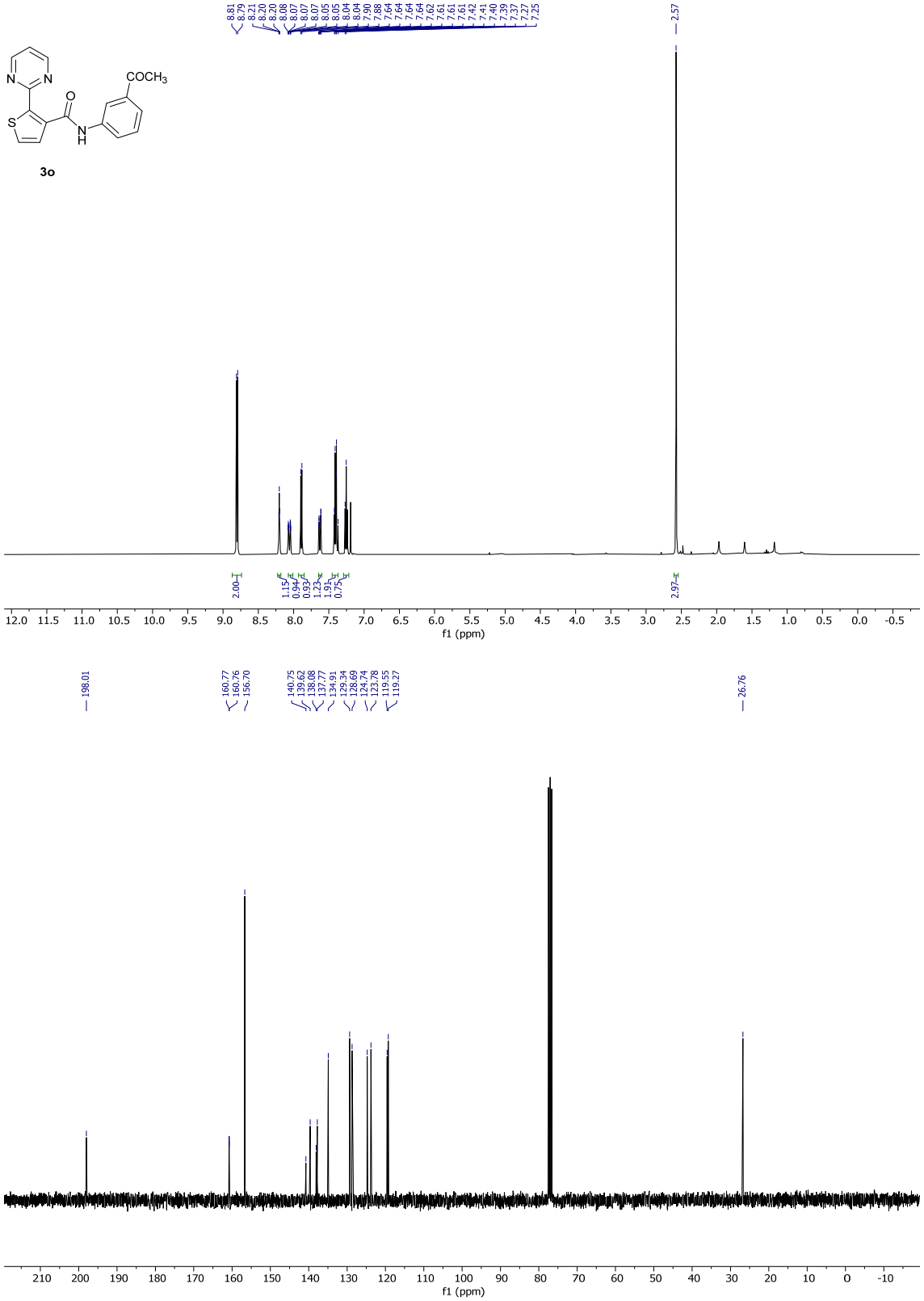


3n

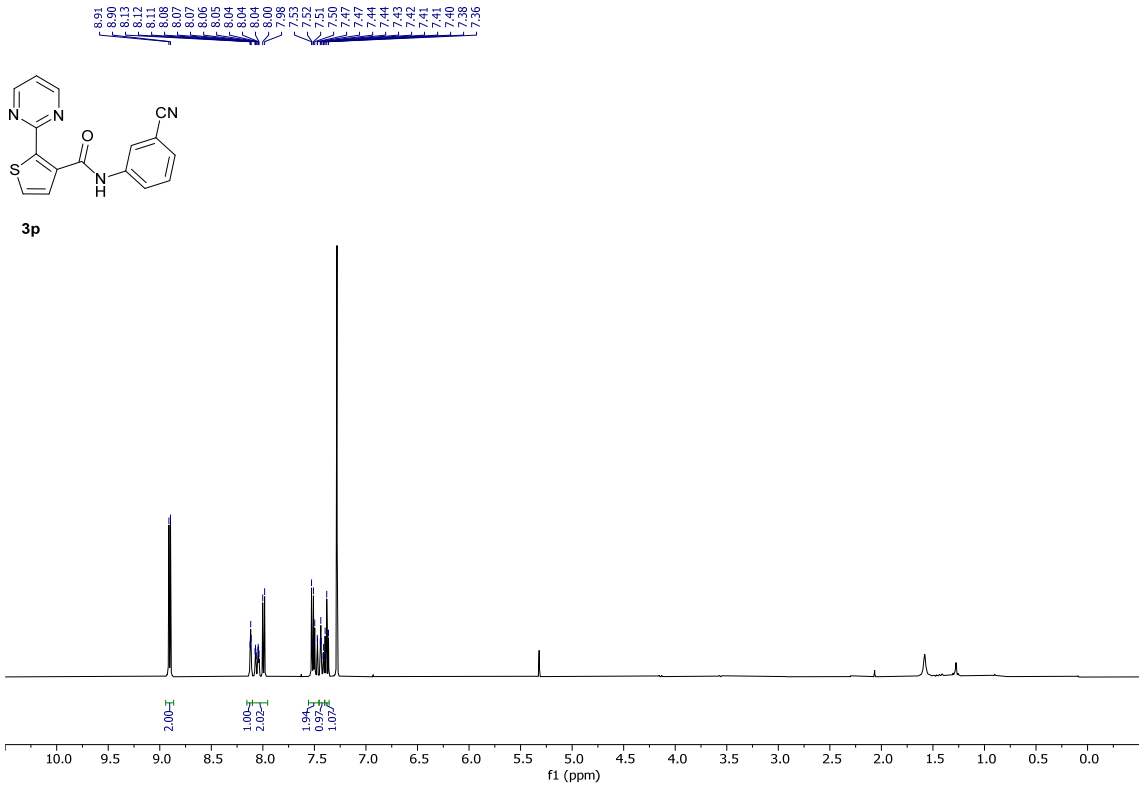


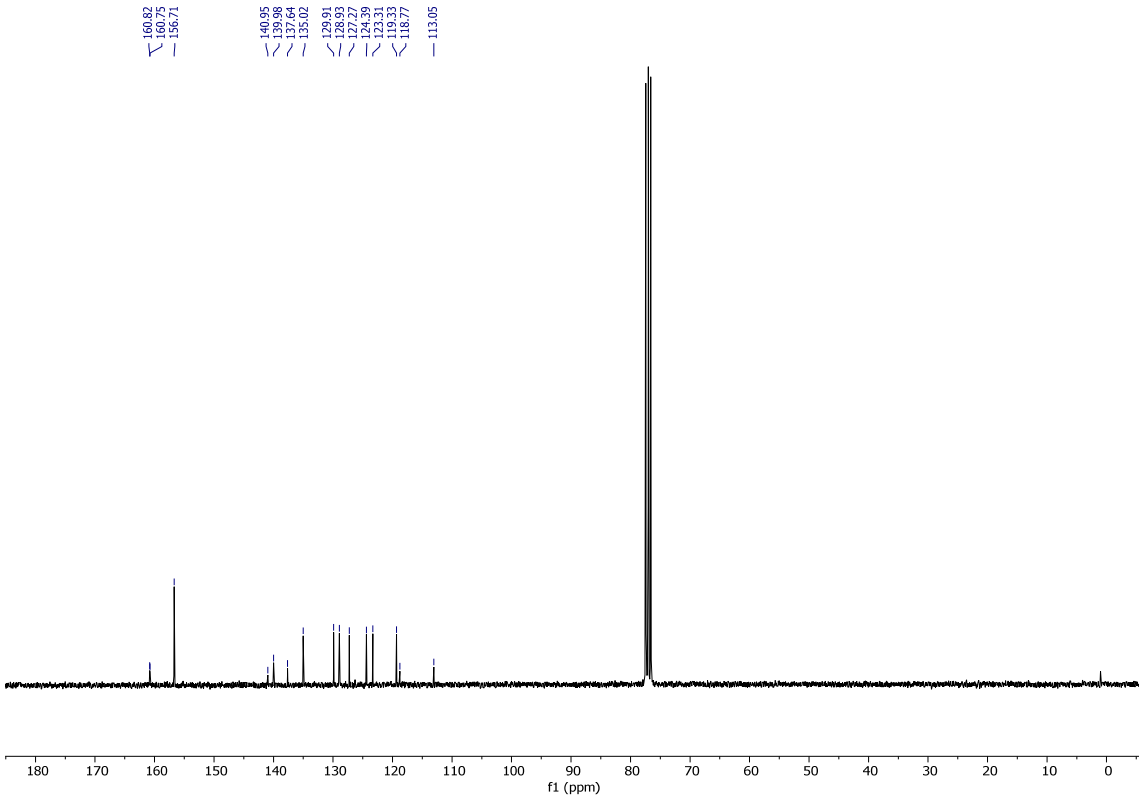


^{1}H and $^{13}C\{^{1}H\}$-NMR spectra of **3n**

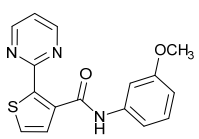


^{1}H and $^{13}C\{^{1}H\}$-NMR spectra of **3o**

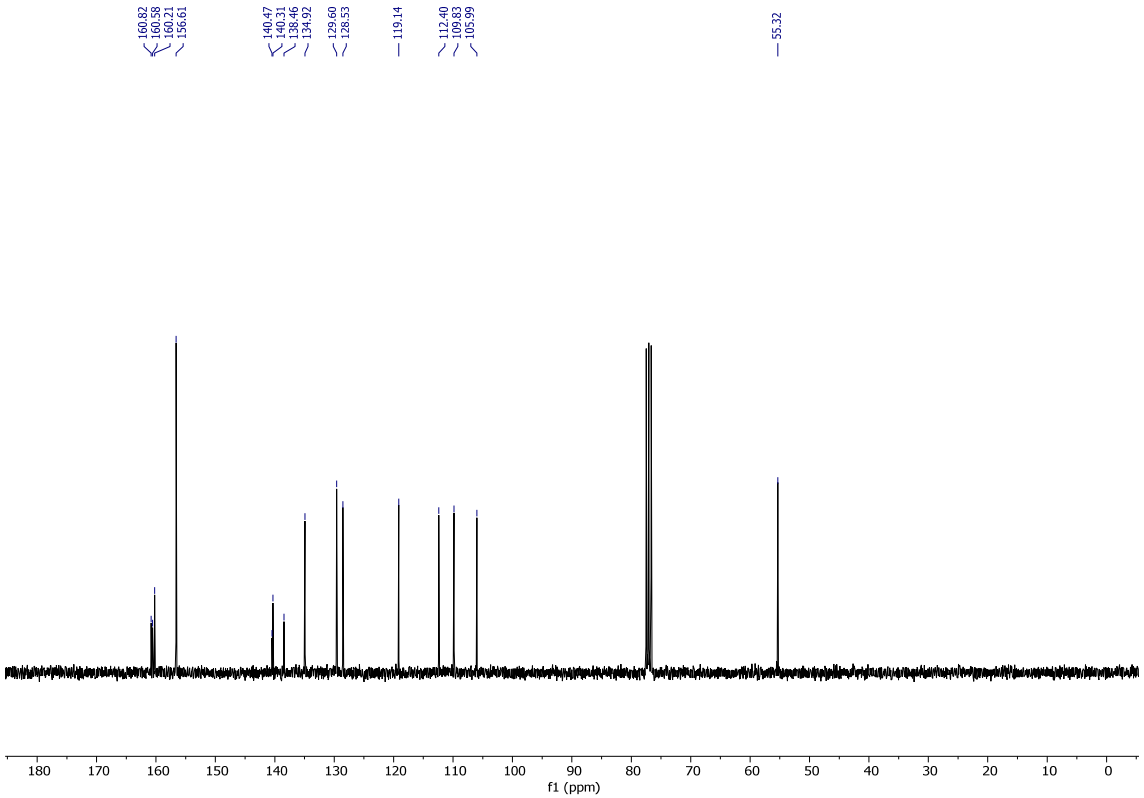




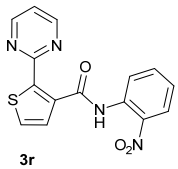
^{1}H and ^{13}C{^{1}H}-NMR spectra of **3p**



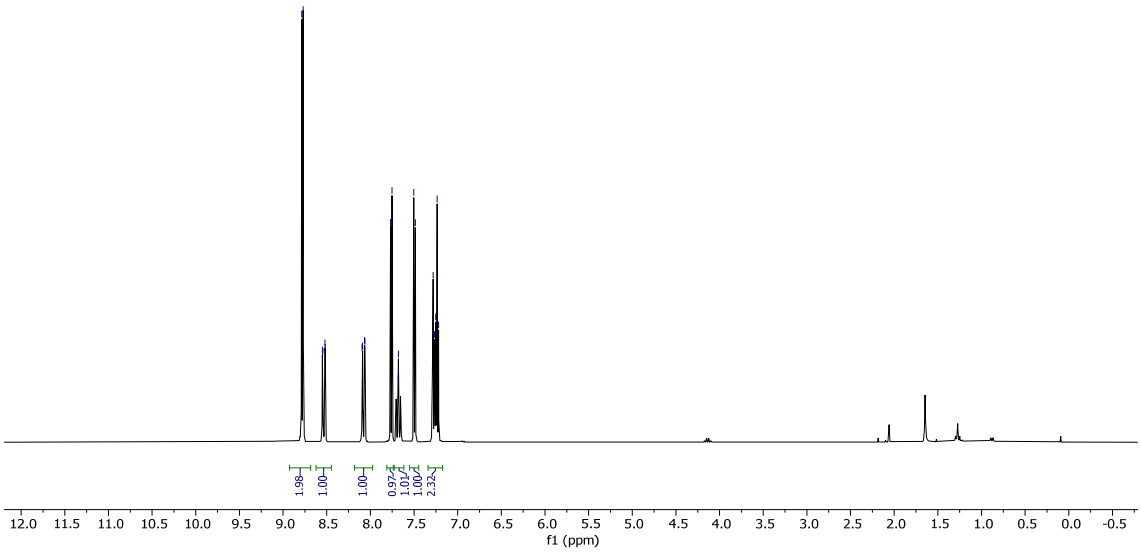
3q

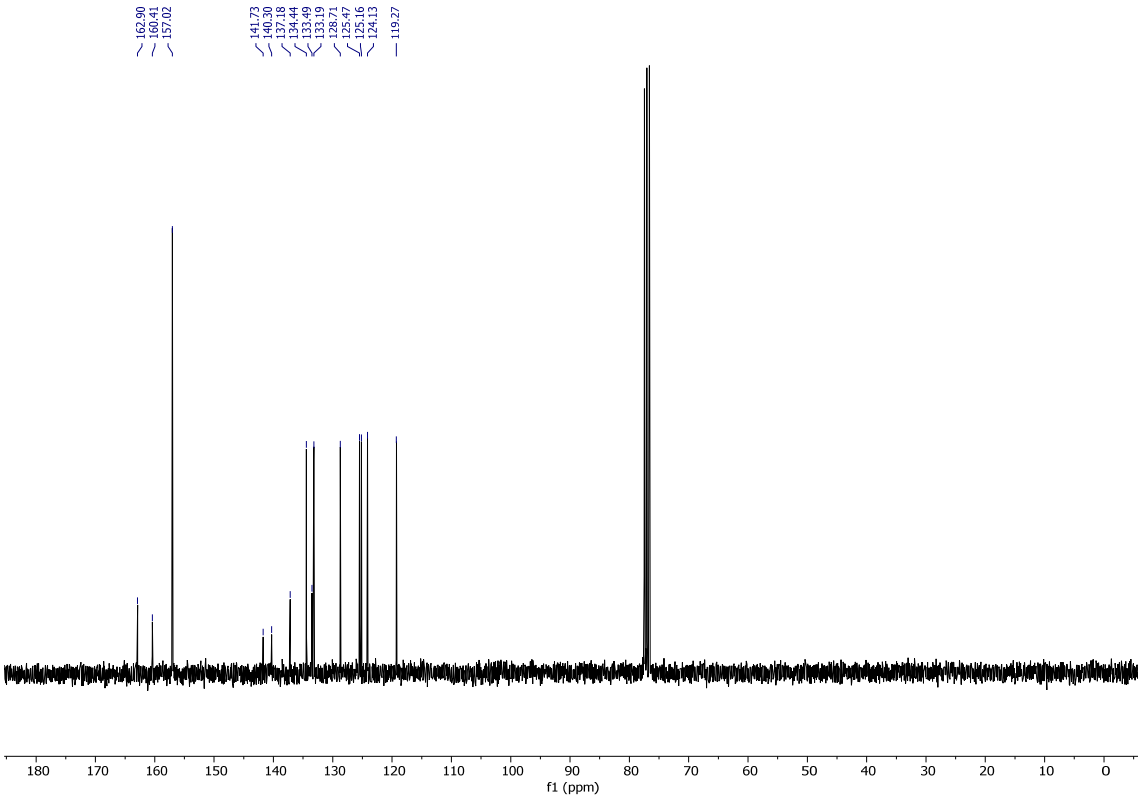


^{1}H and ^{13}C{^{1}H}-NMR spectra of **3q**

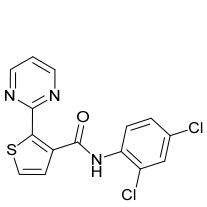


3r

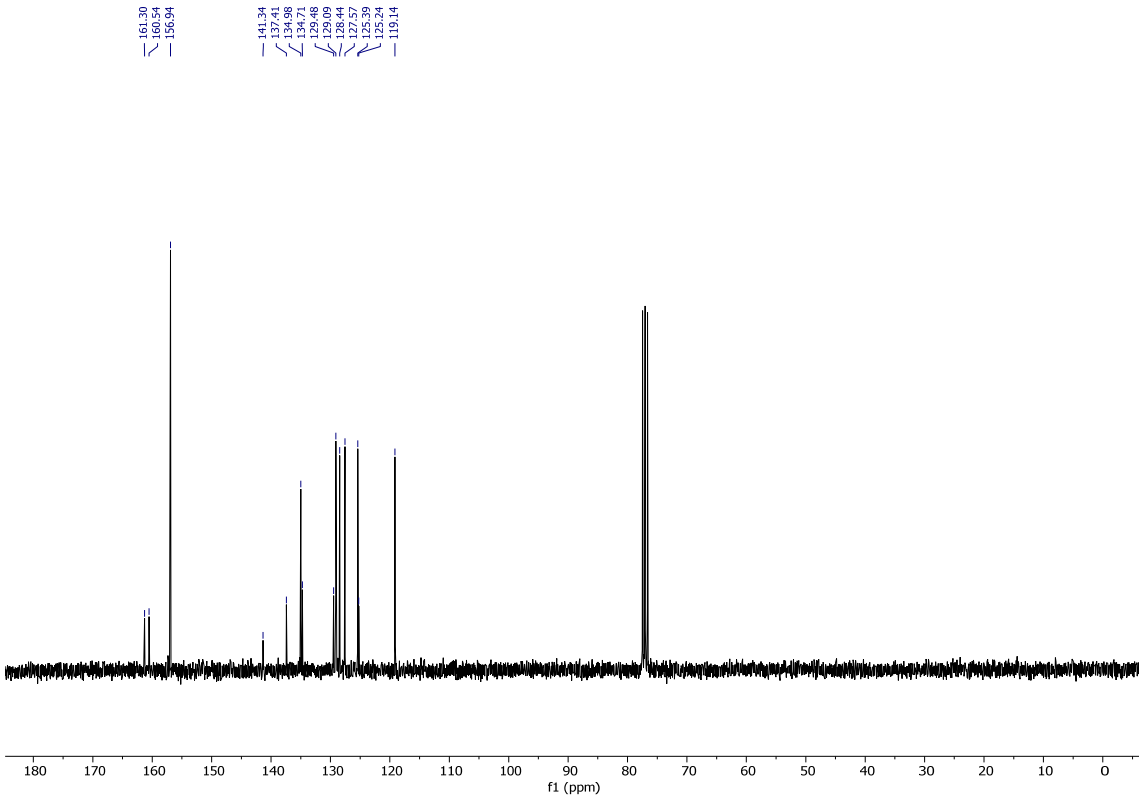




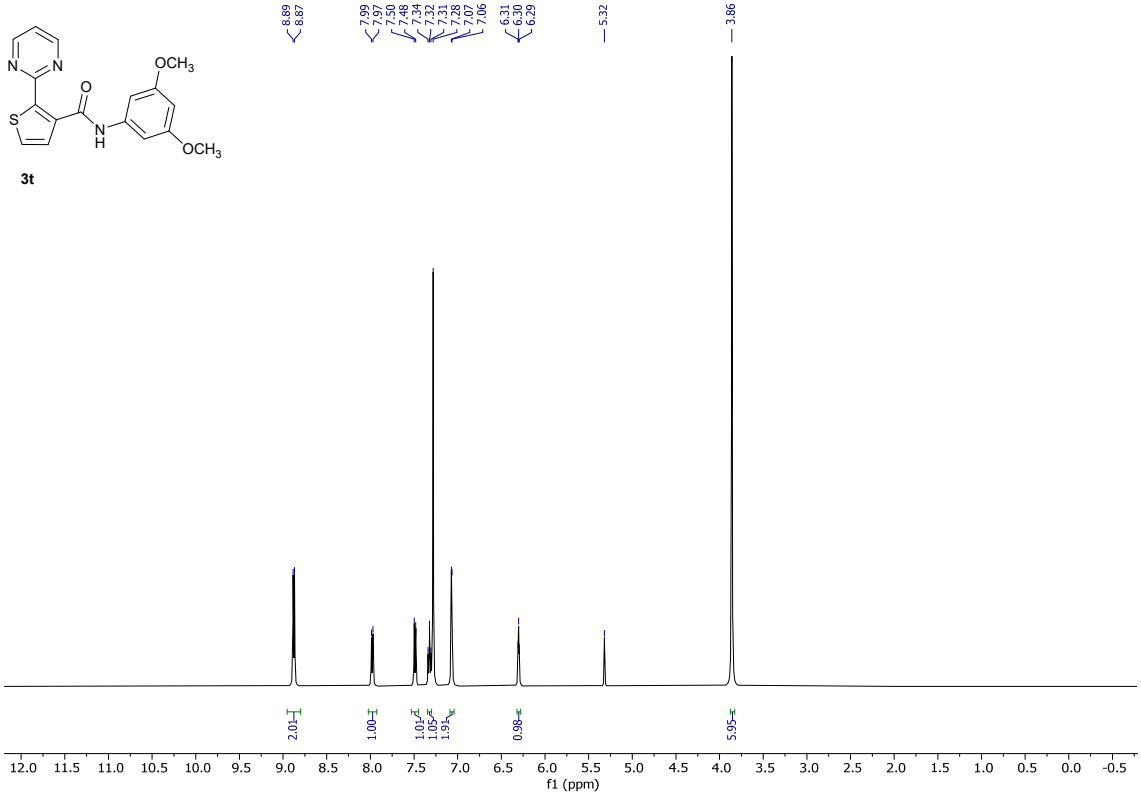
^{1}H and $^{13}C\{^{1}H\}$-NMR spectra of **3r**

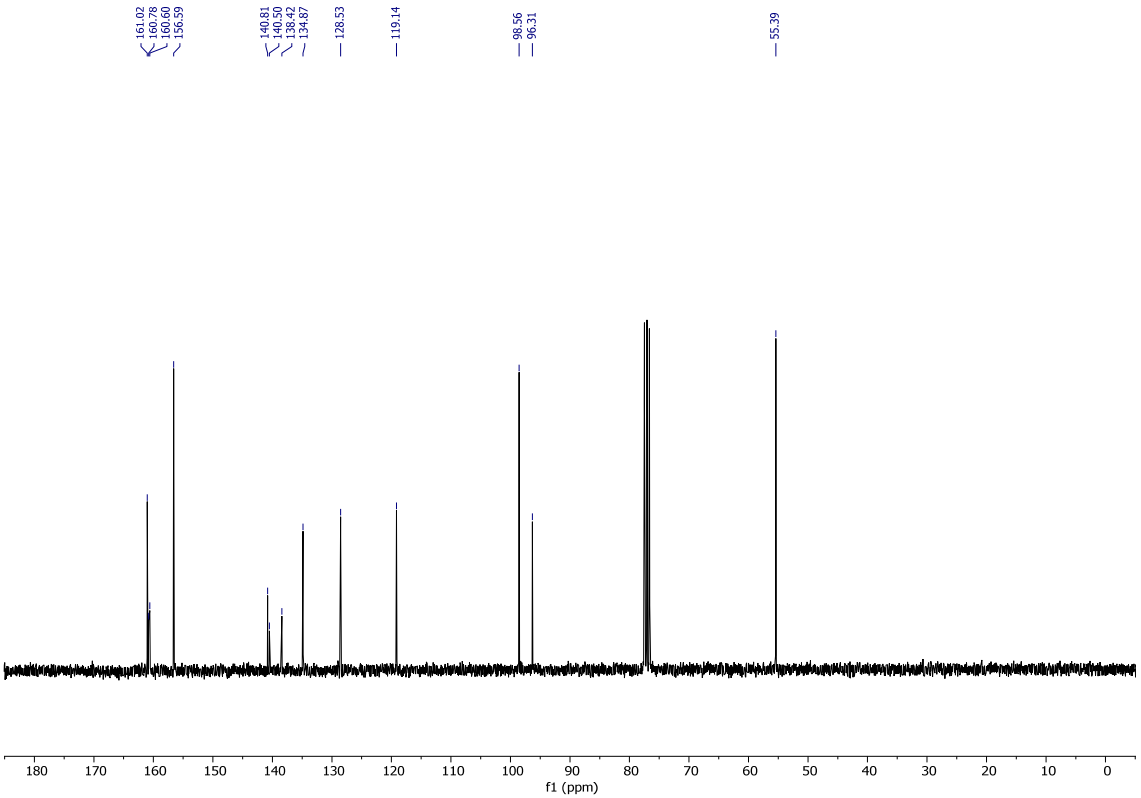


3s



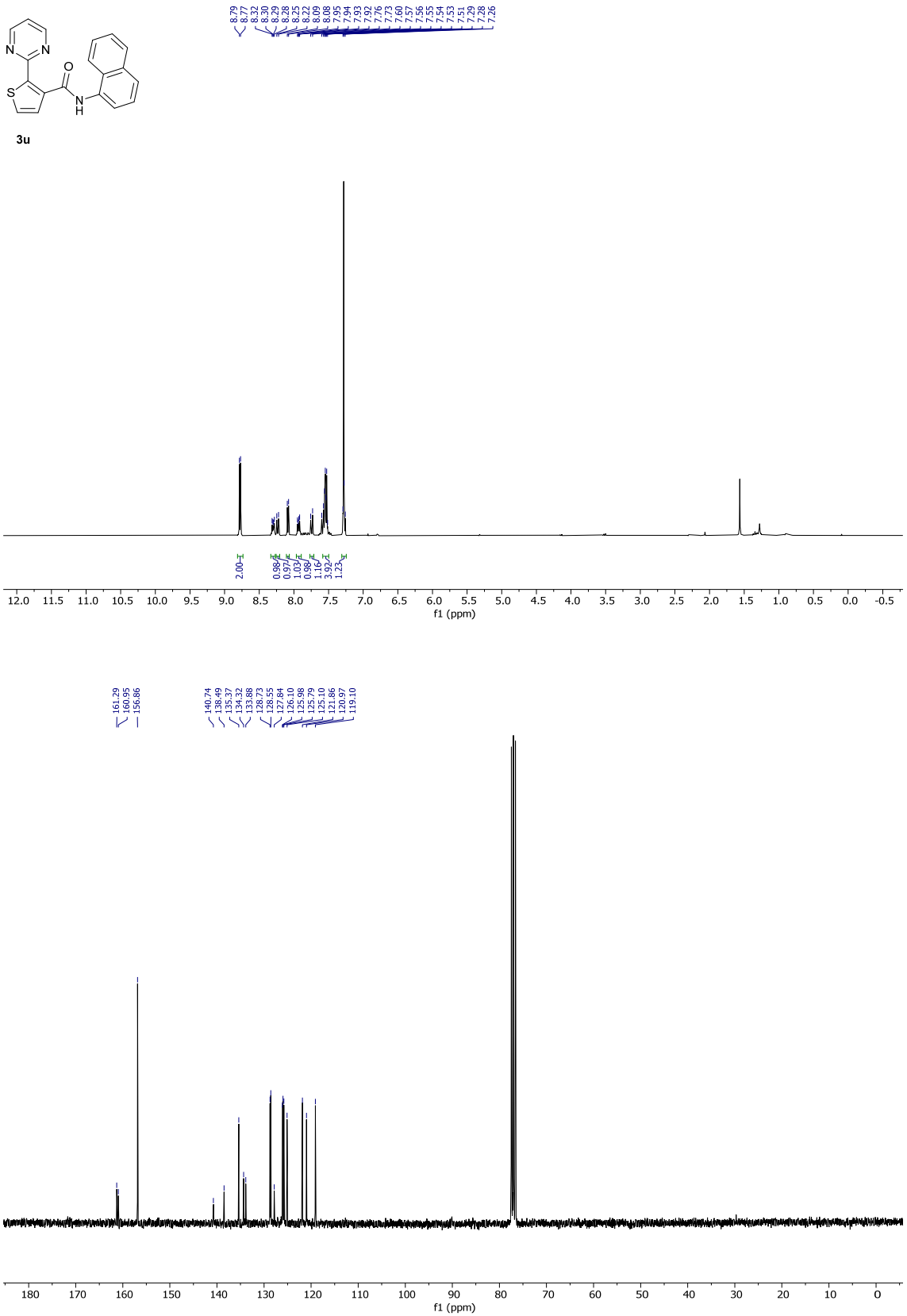
^{1}H and $^{13}C\{^{1}H\}$-NMR spectra of **3s**



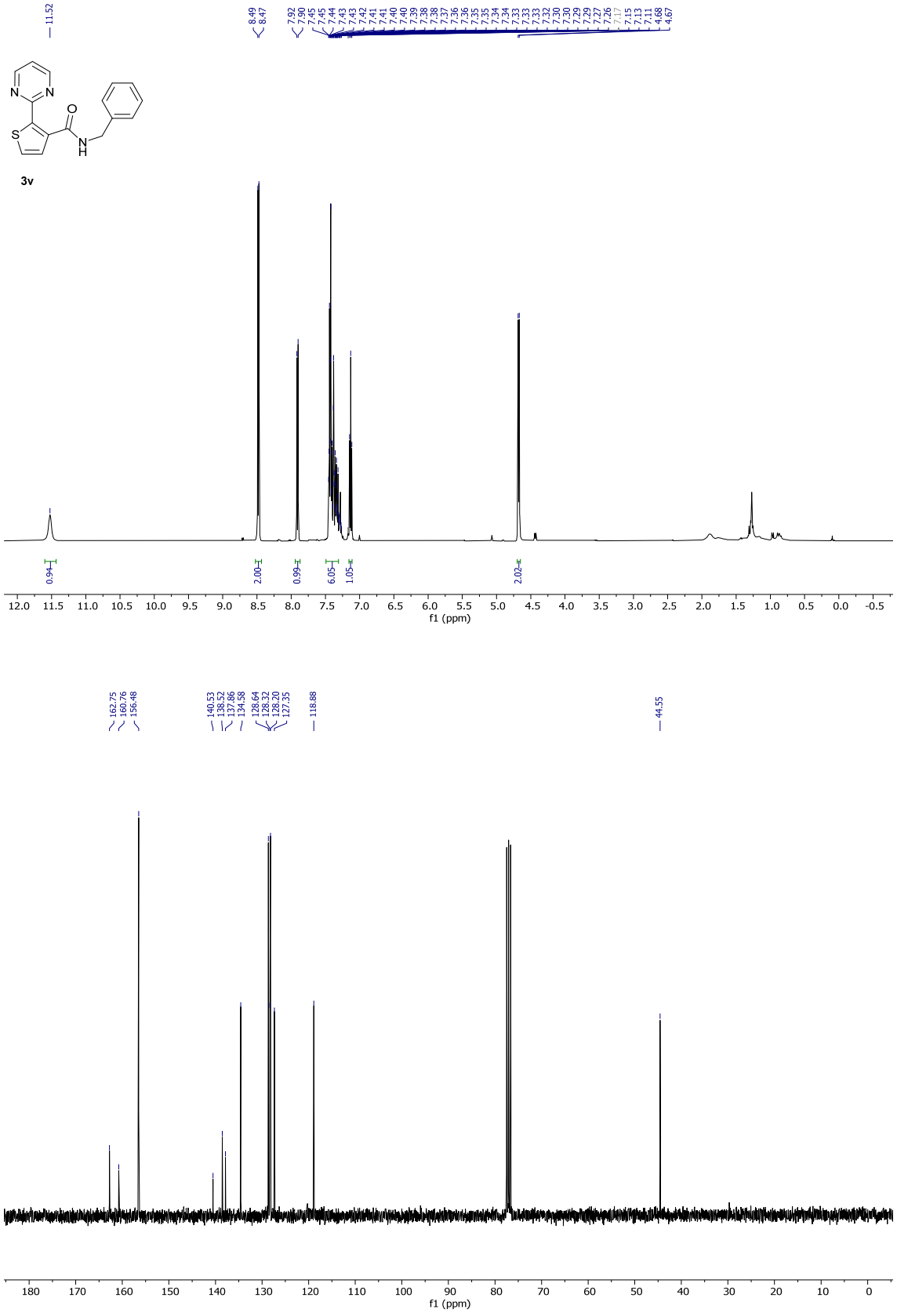


3t

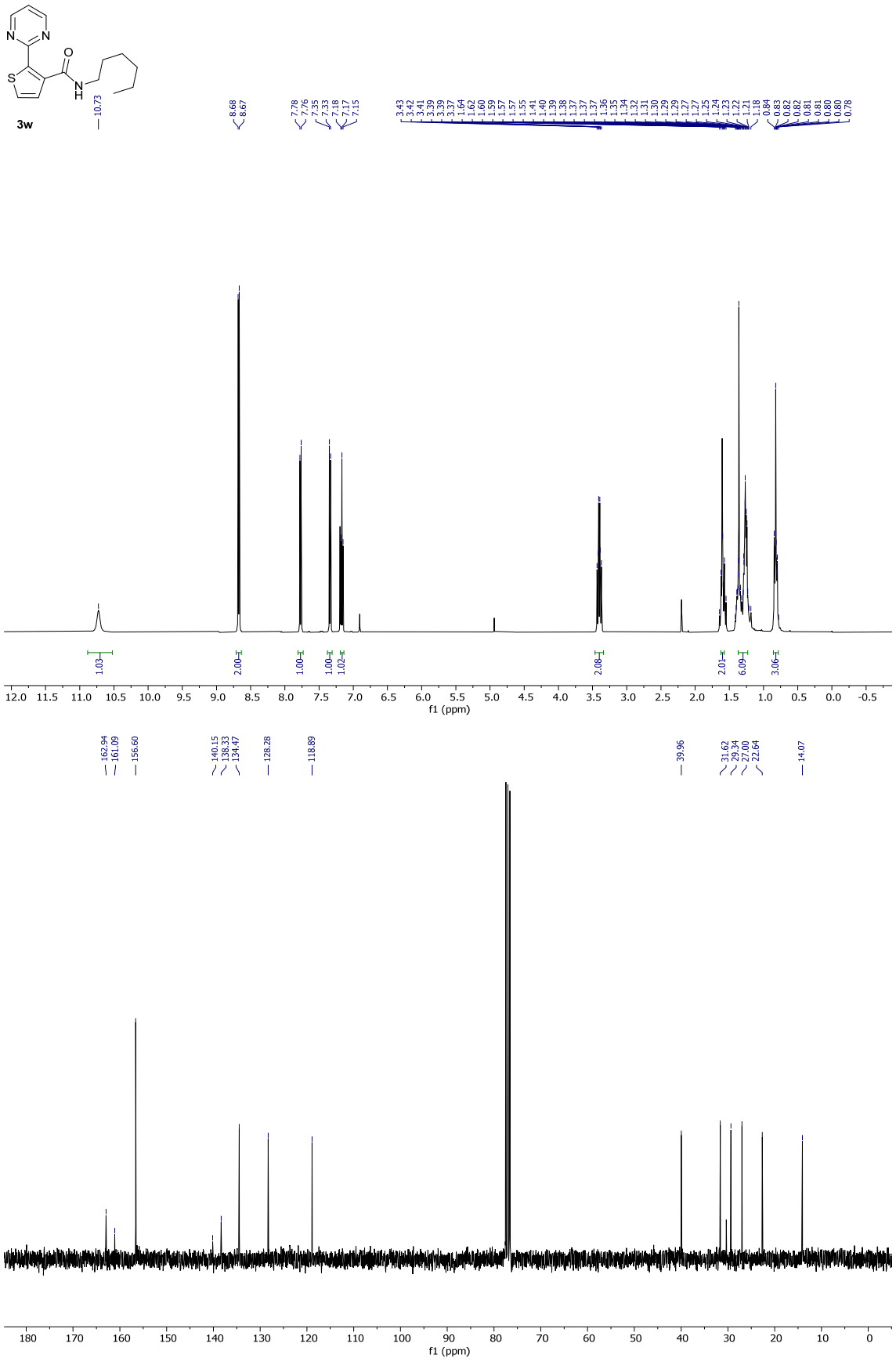
^{1}H and $^{13}C\{^{1}H\}$-NMR spectra of **3t**



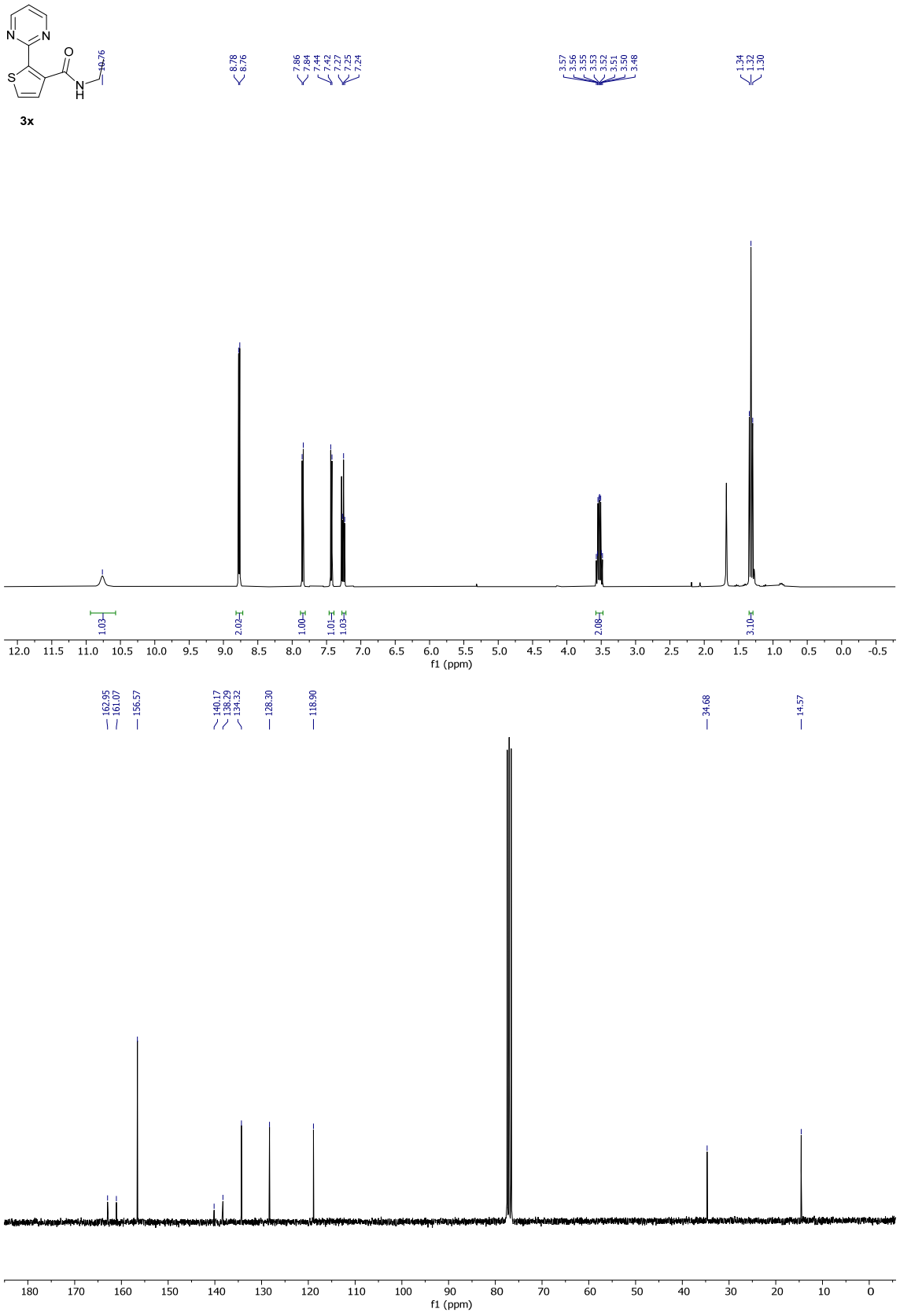
^{1}H and ^{13}C{^{1}H}-NMR spectra of **3u**



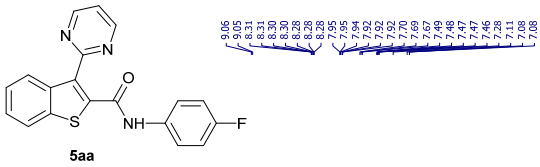
^{1}H and ^{13}C{^{1}H}-NMR spectra of **3v**



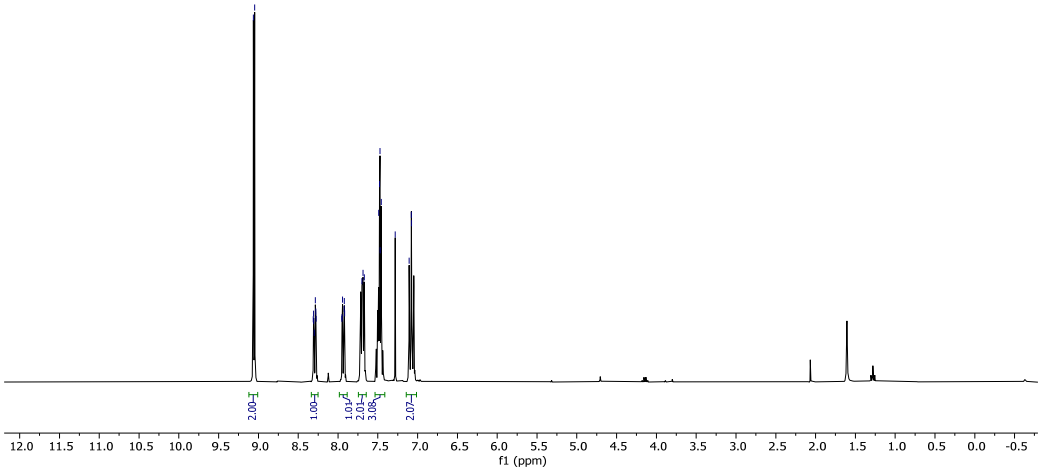
^{1}H and $^{13}C\{^{1}H\}$-NMR spectra of **3w**

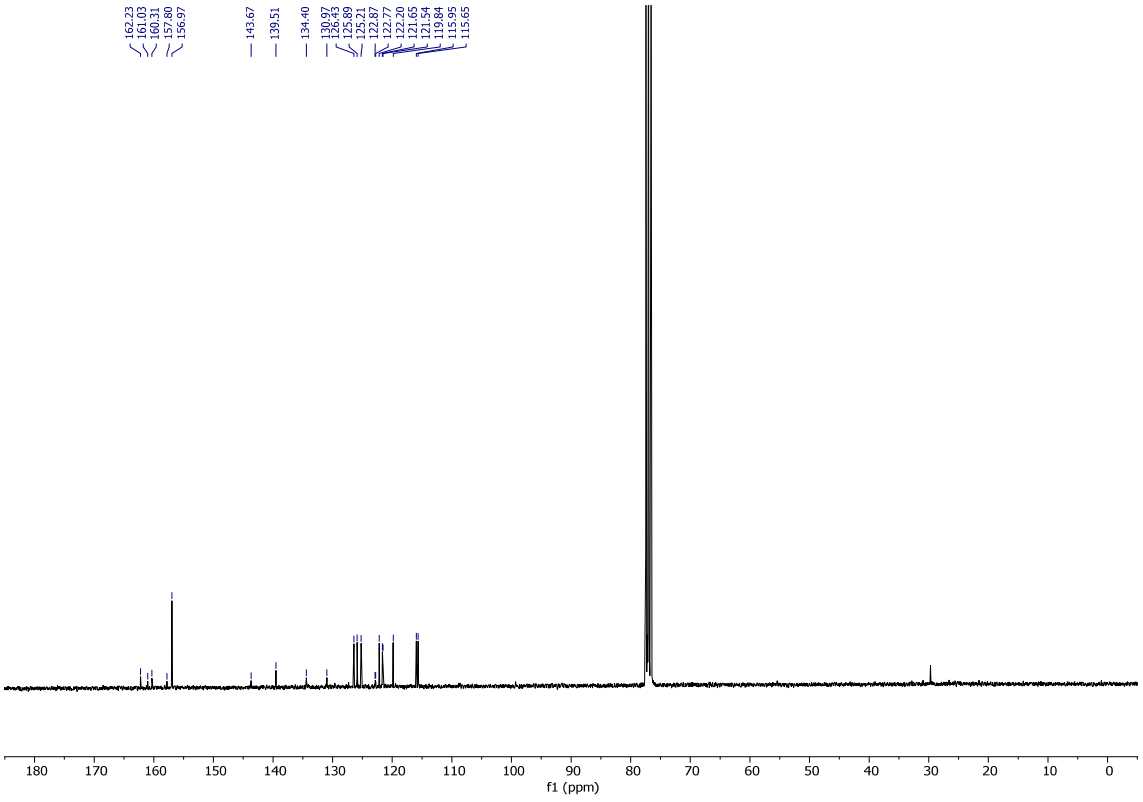


^{1}H and ^{13}C{^{1}H}-NMR spectra of **3x**

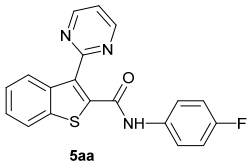


5aa

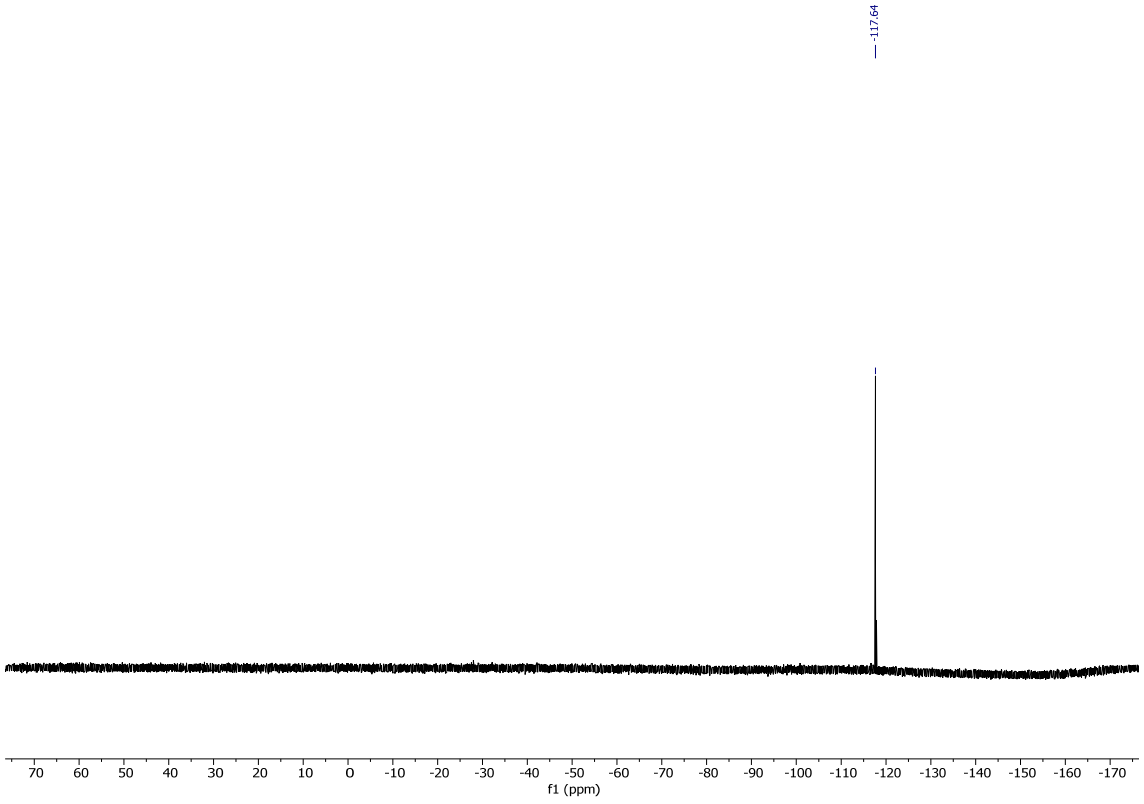




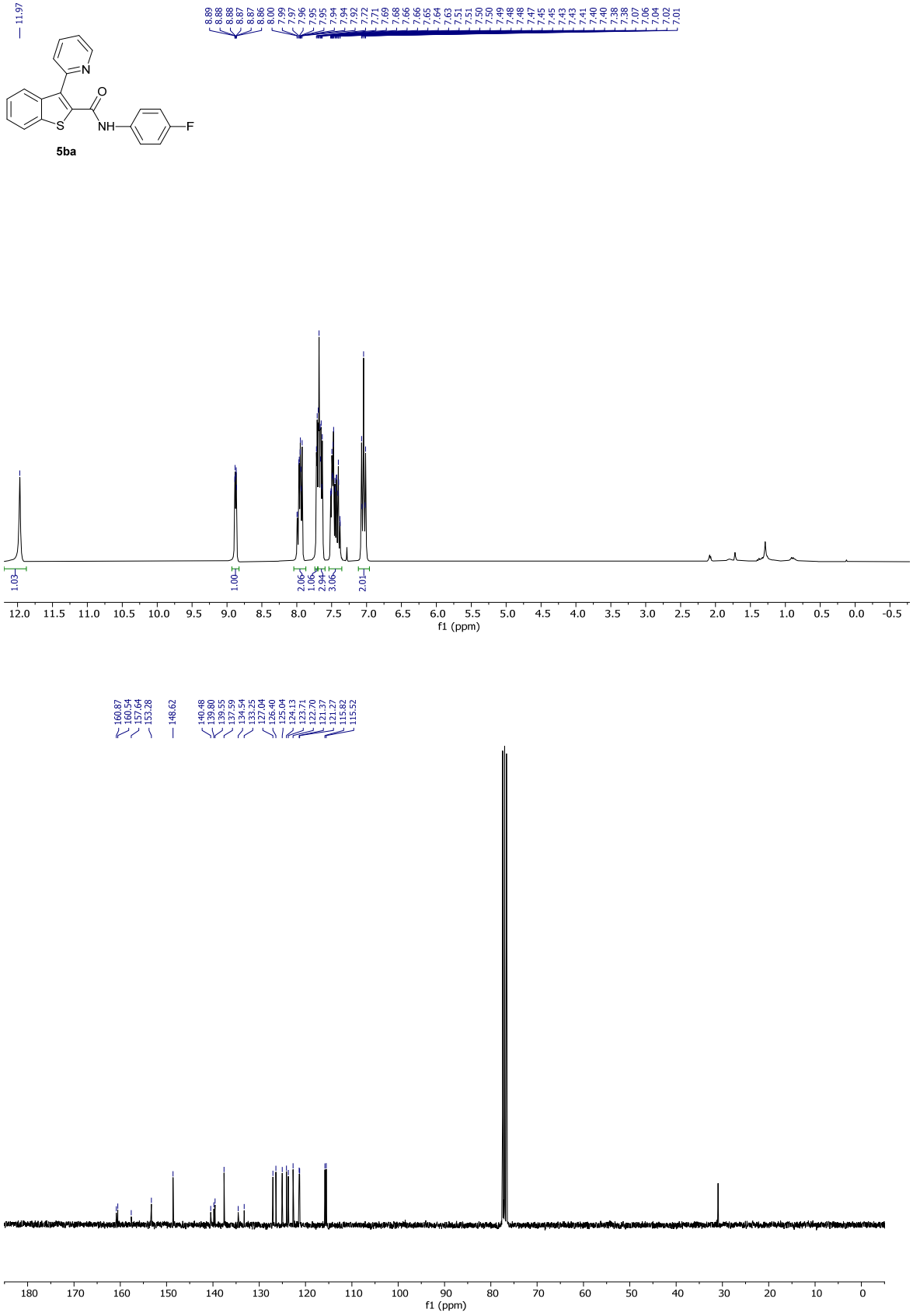
^{1}H and $^{13}C\{^{1}H\}$-NMR spectra of **5aa**



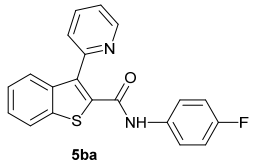
5aa



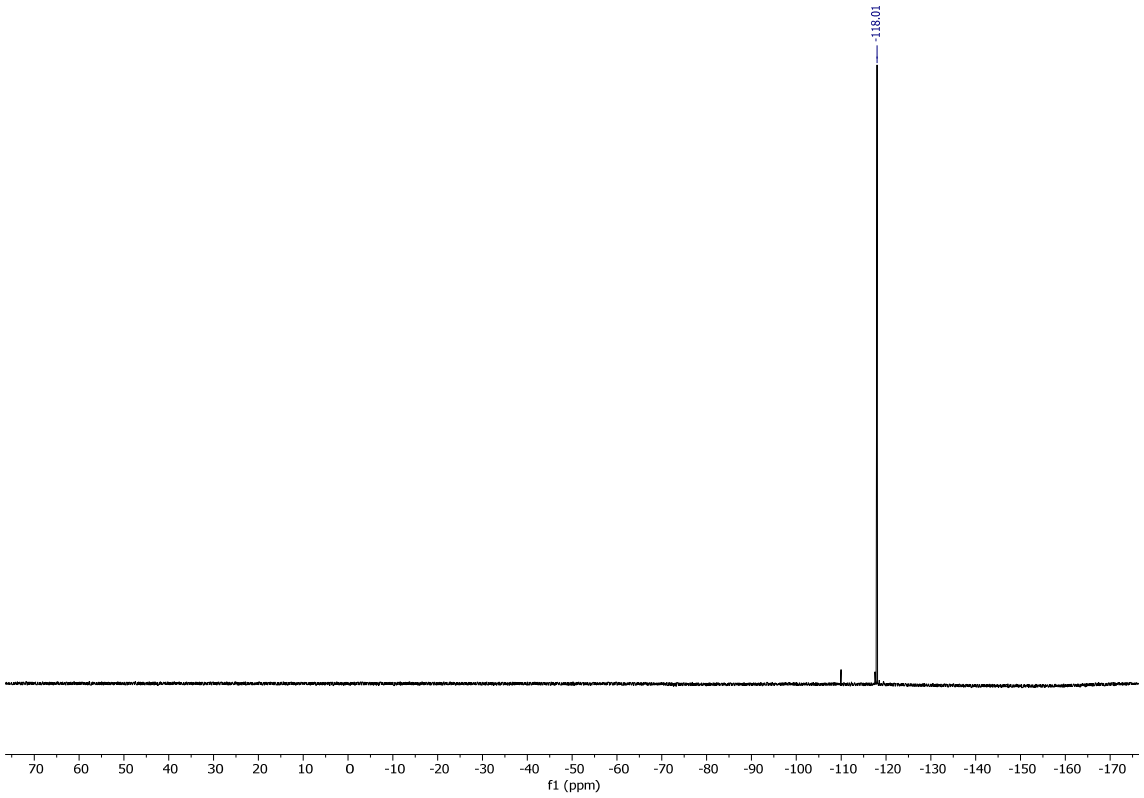
^{19}F NMR spectrum of **5aa**



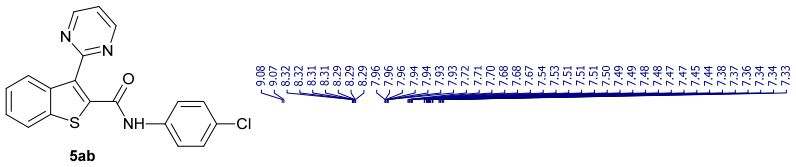
^{1}H and ^{13}C{^{1}H}-NMR spectra of **5ba**



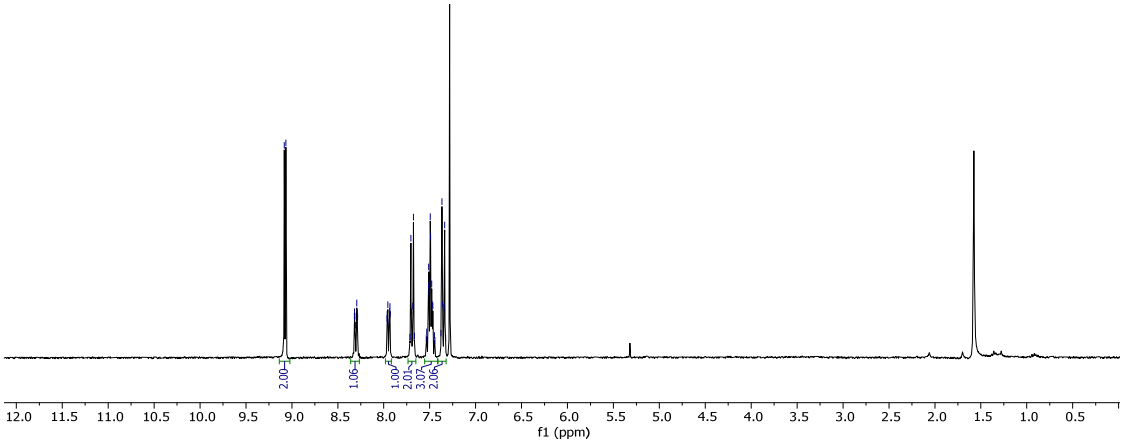
5ba

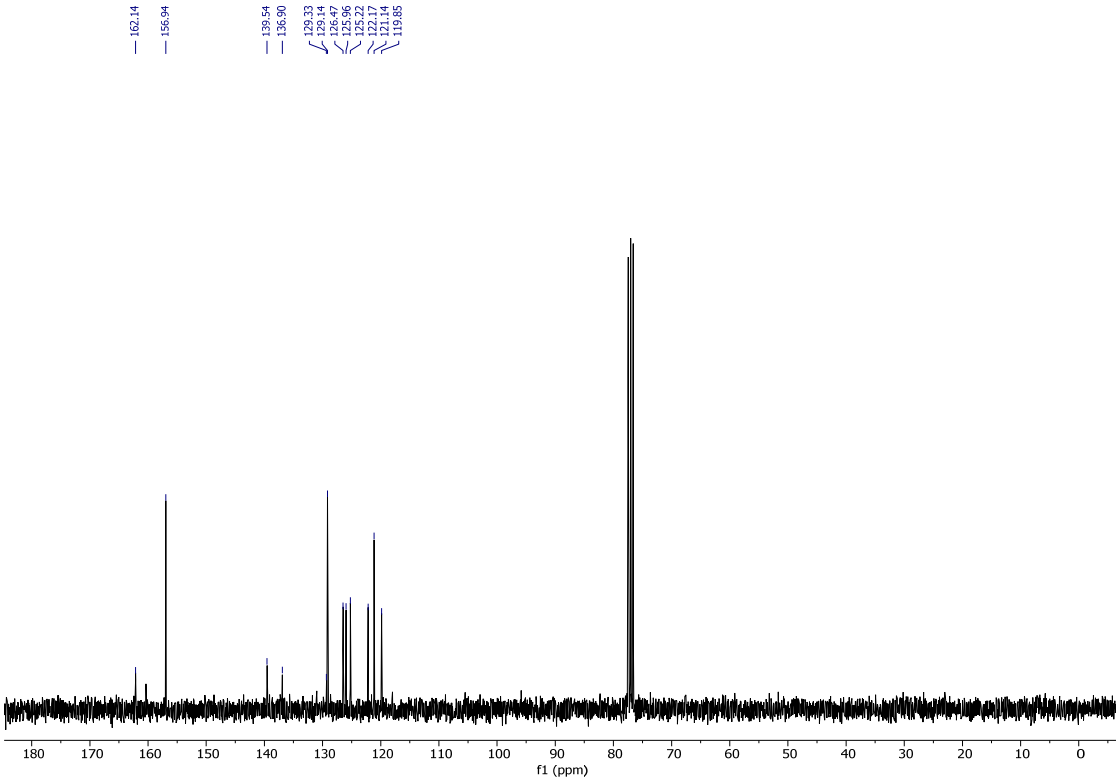


^{19}F NMR spectrum of **5ba**

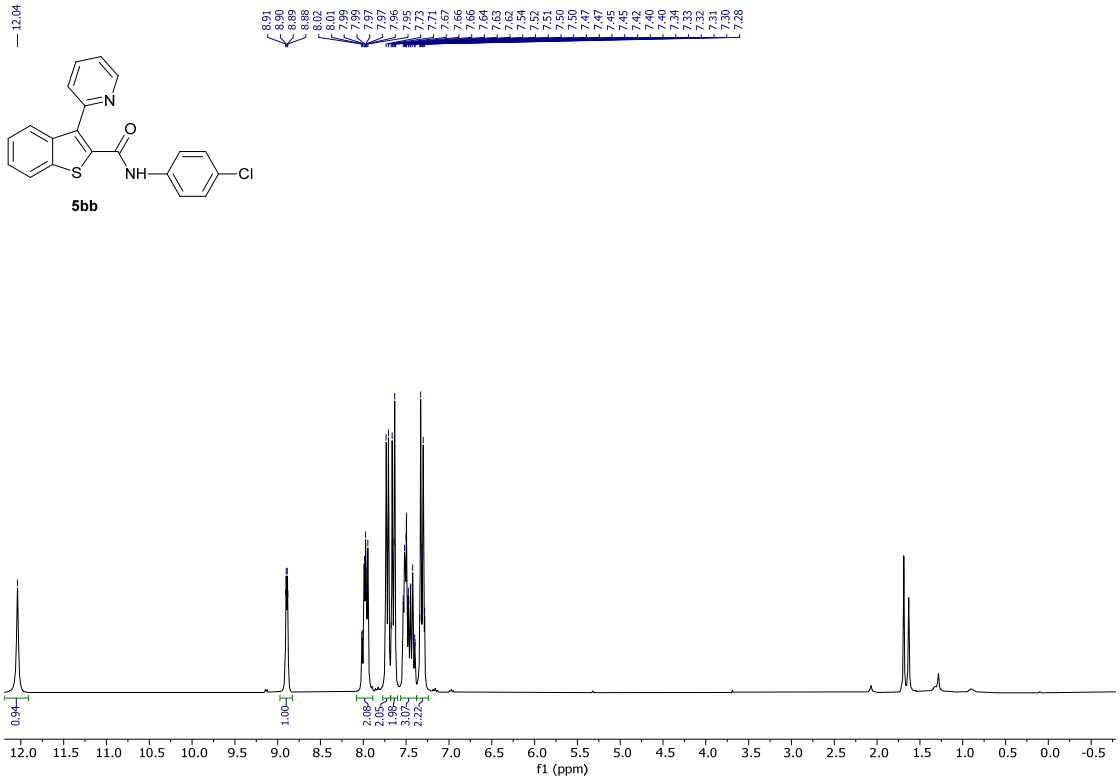


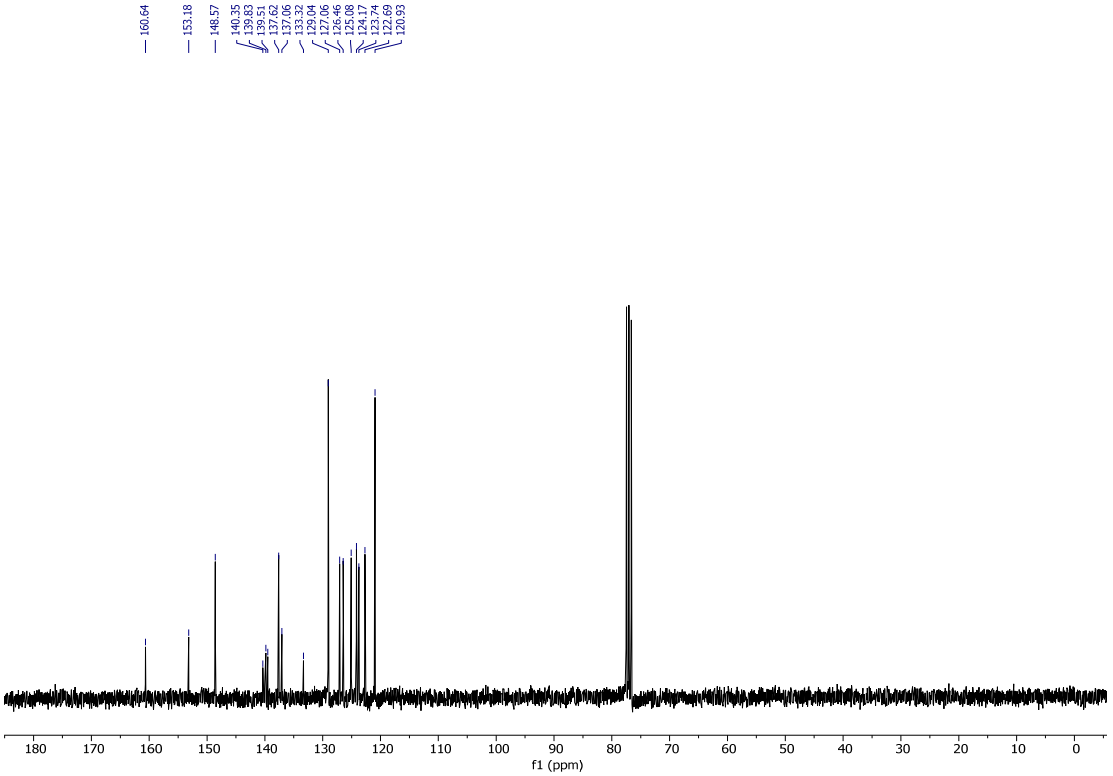
5ab



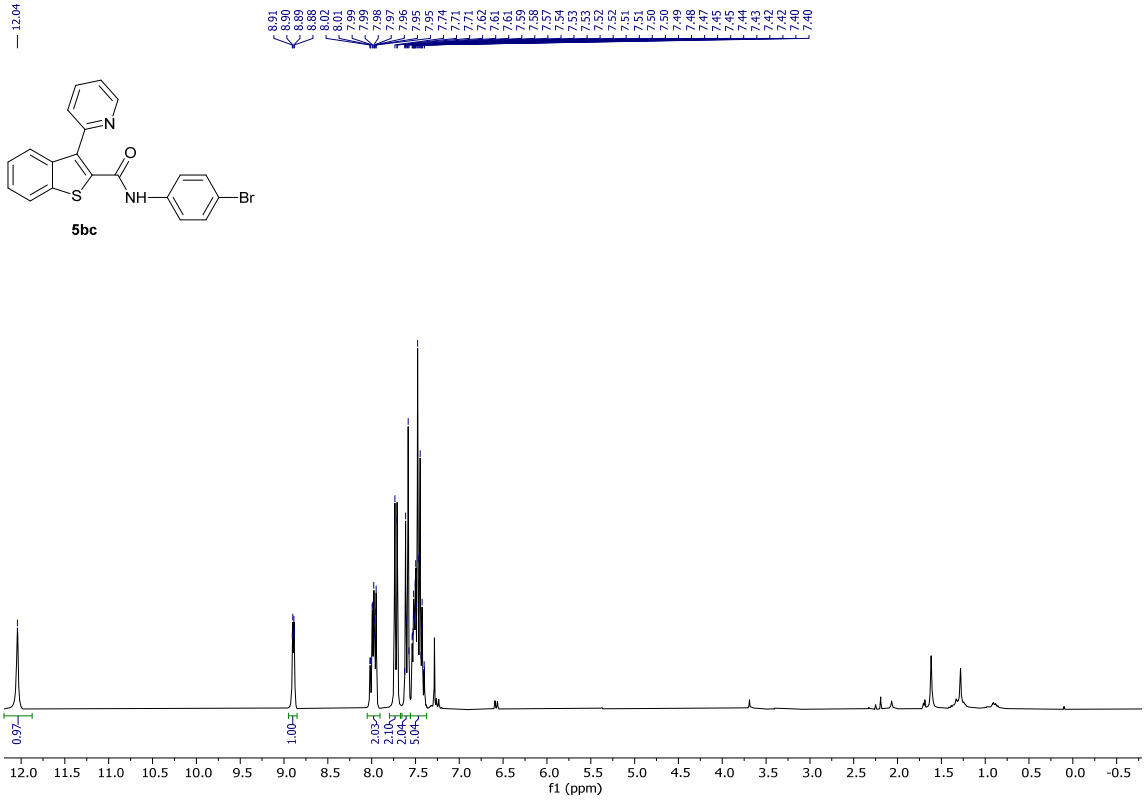


^{1}H and ^{13}C{^{1}H}-NMR spectra of **5ab**

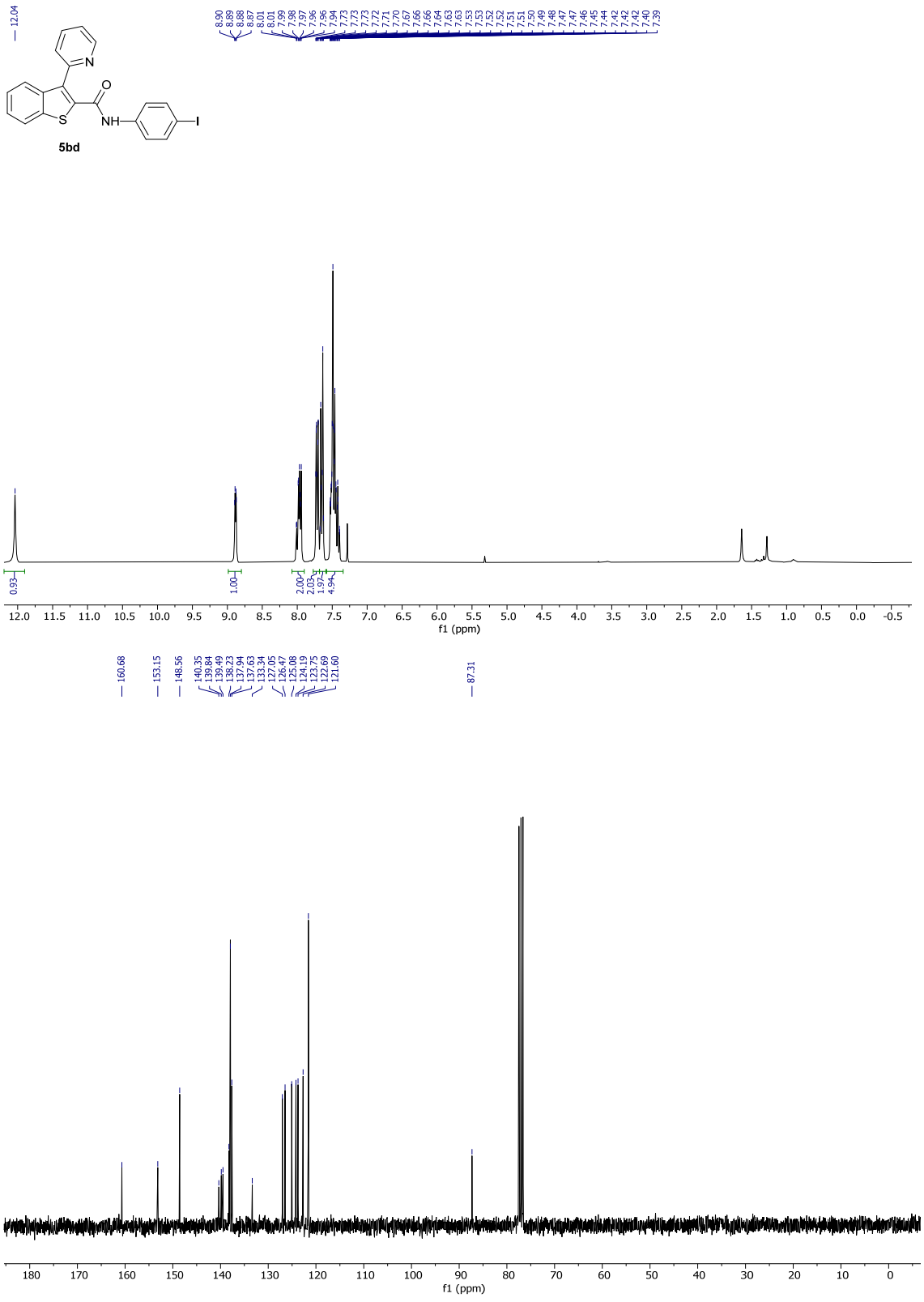




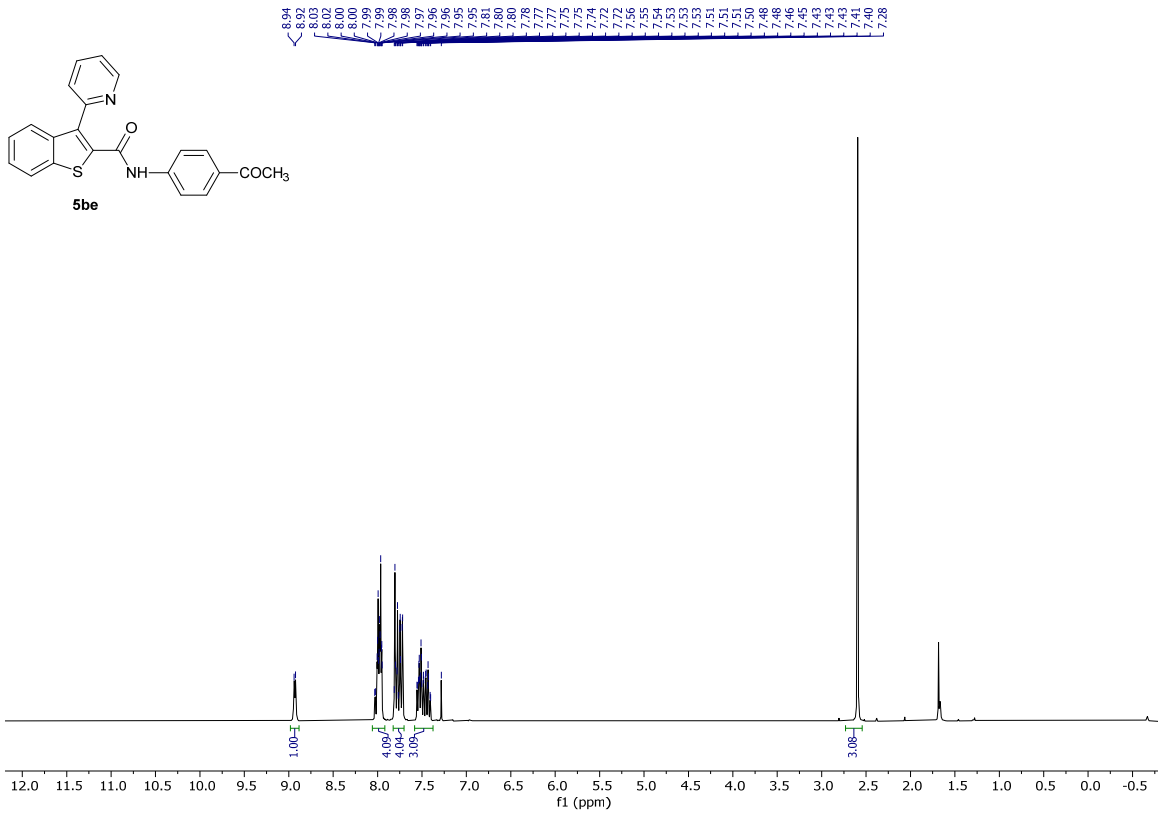
^{1}H and ^{13}C{^{1}H}-NMR spectra of **5bb**

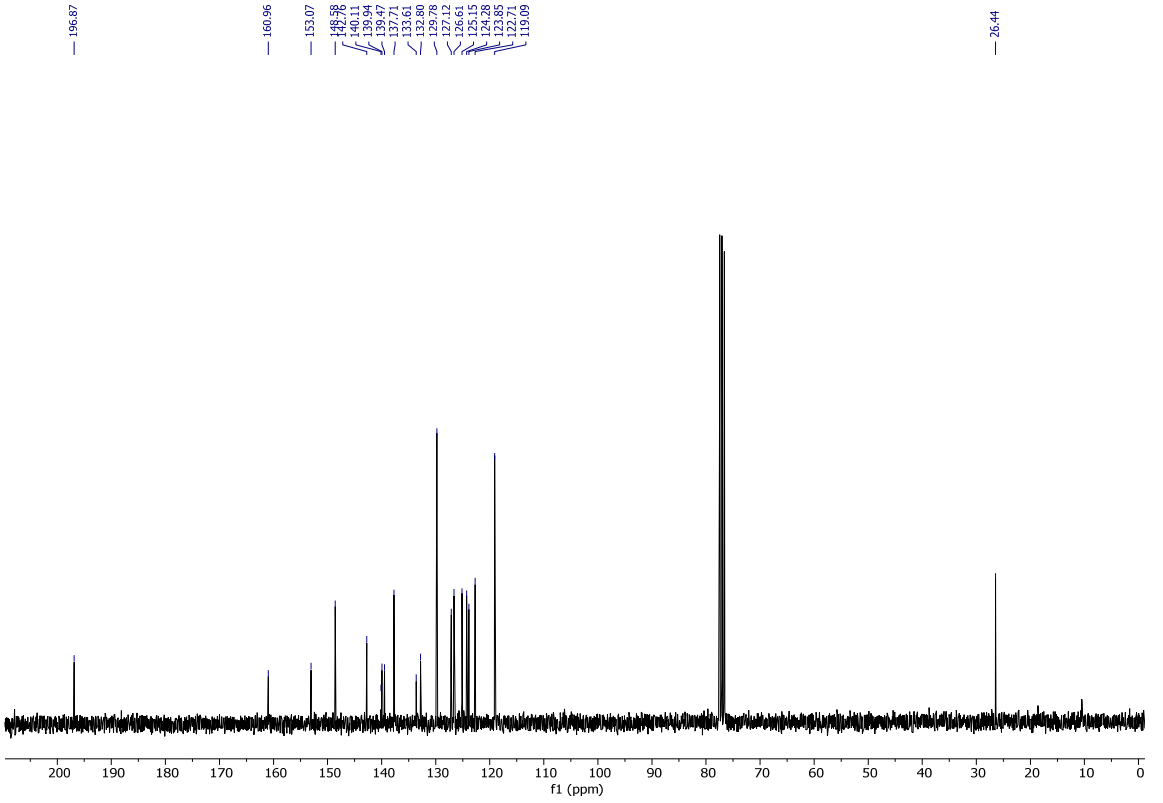


^{1}H and $^{13}C\{^{1}H\}$-NMR spectra of **5bc**

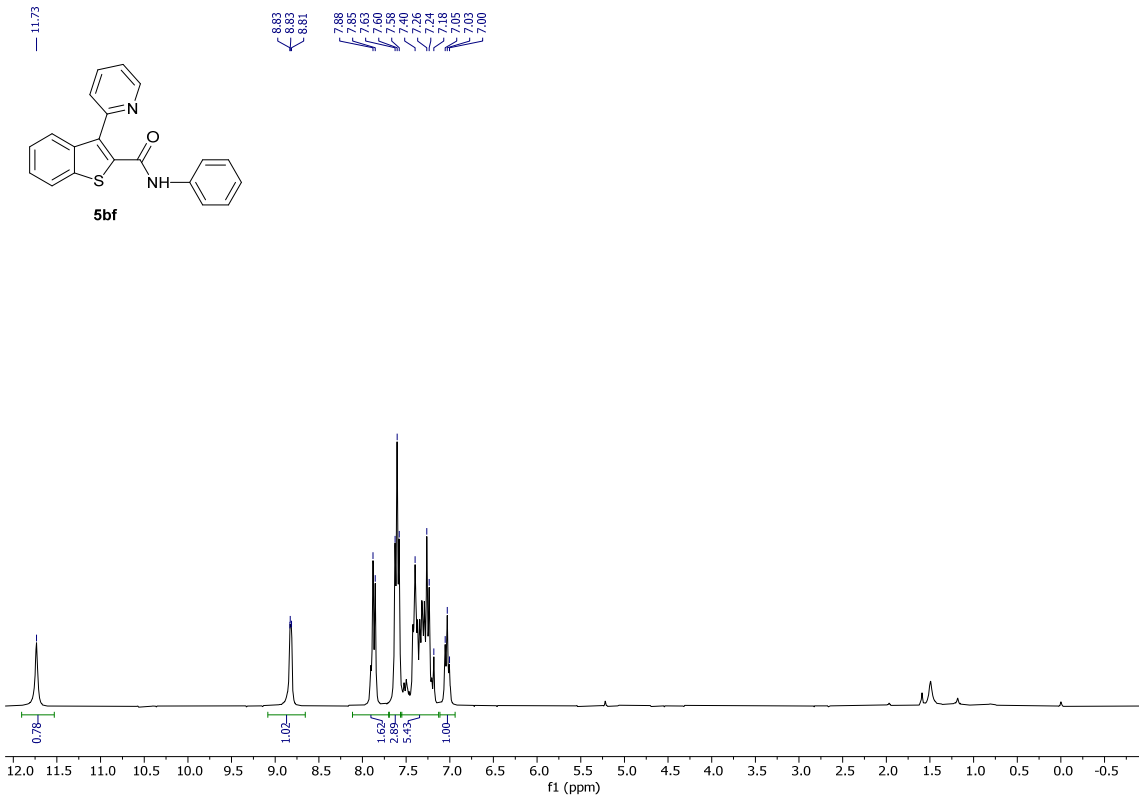


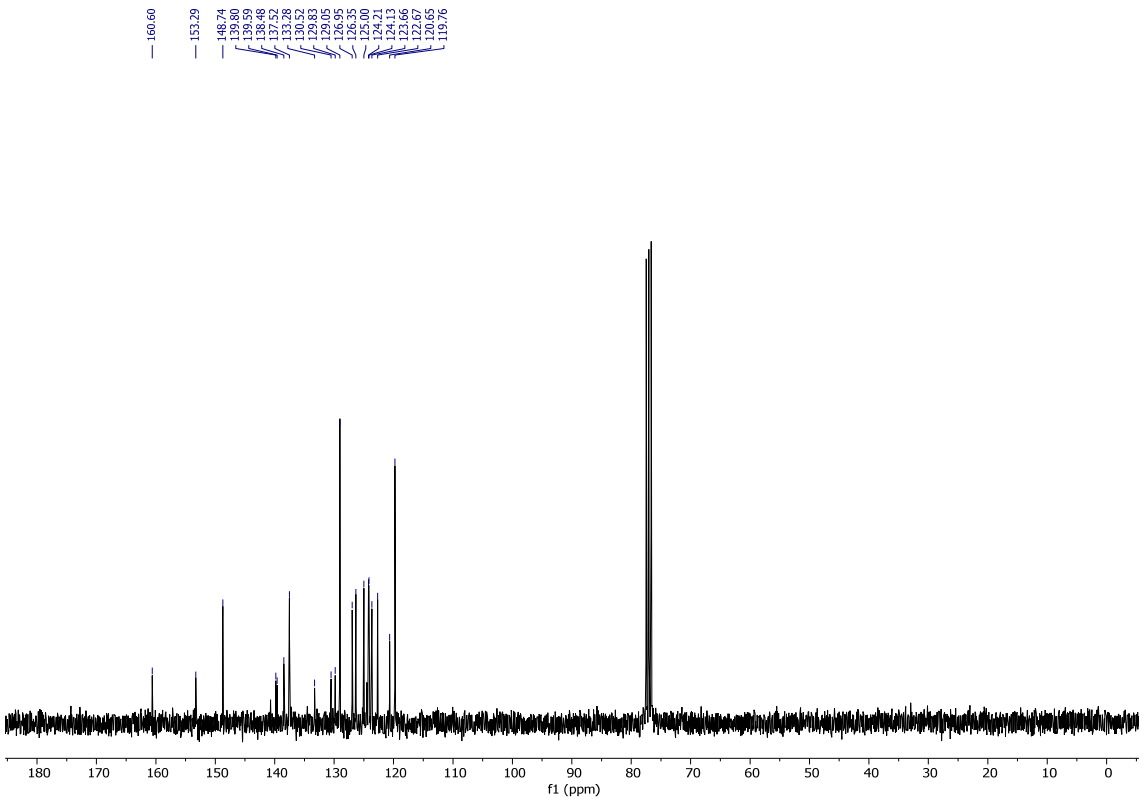
^{1}H and $^{13}C\{^{1}H\}$-NMR spectra of **5bd**



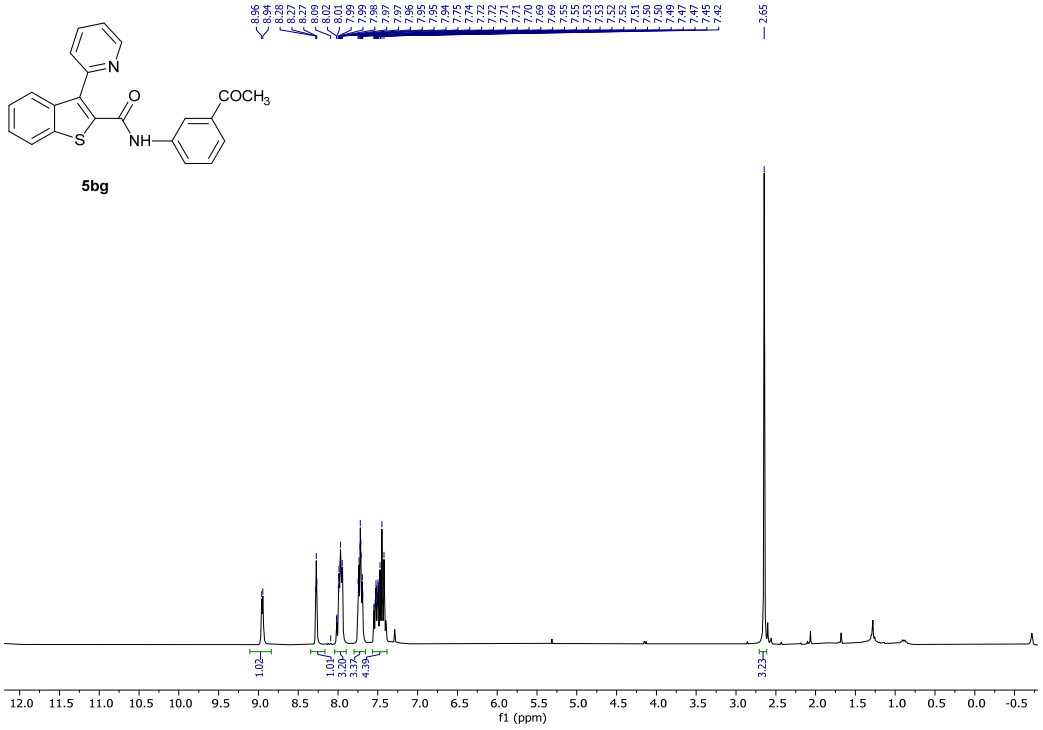


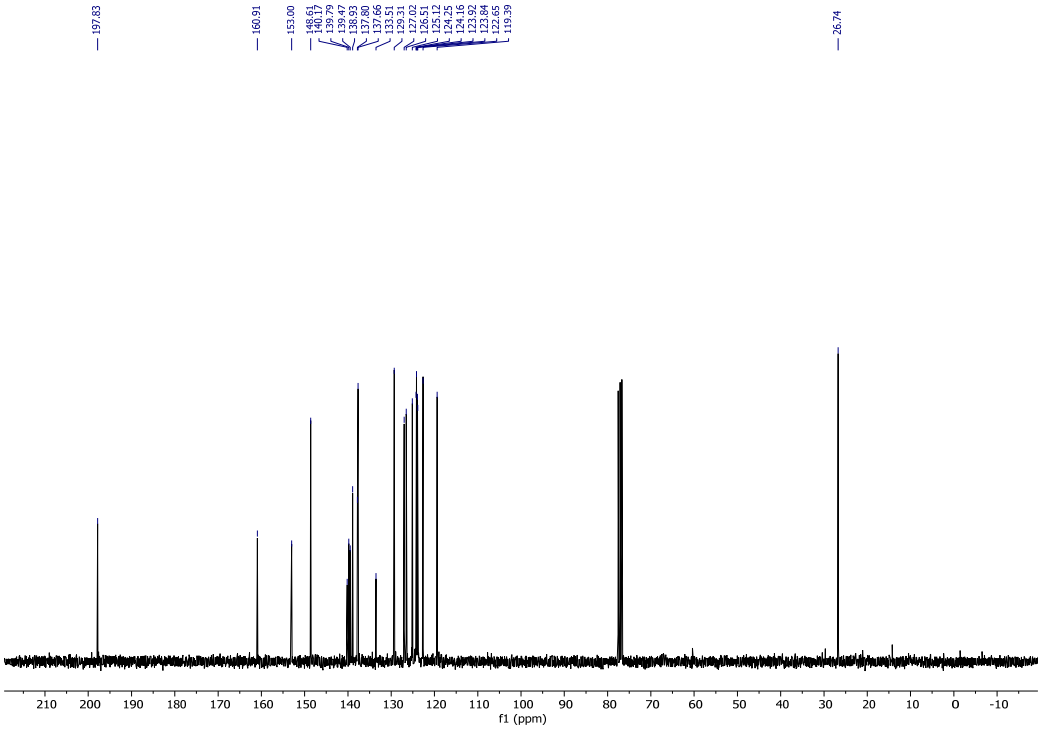
^{1}H and $^{13}C\{^{1}H\}$-NMR spectra of **5be**



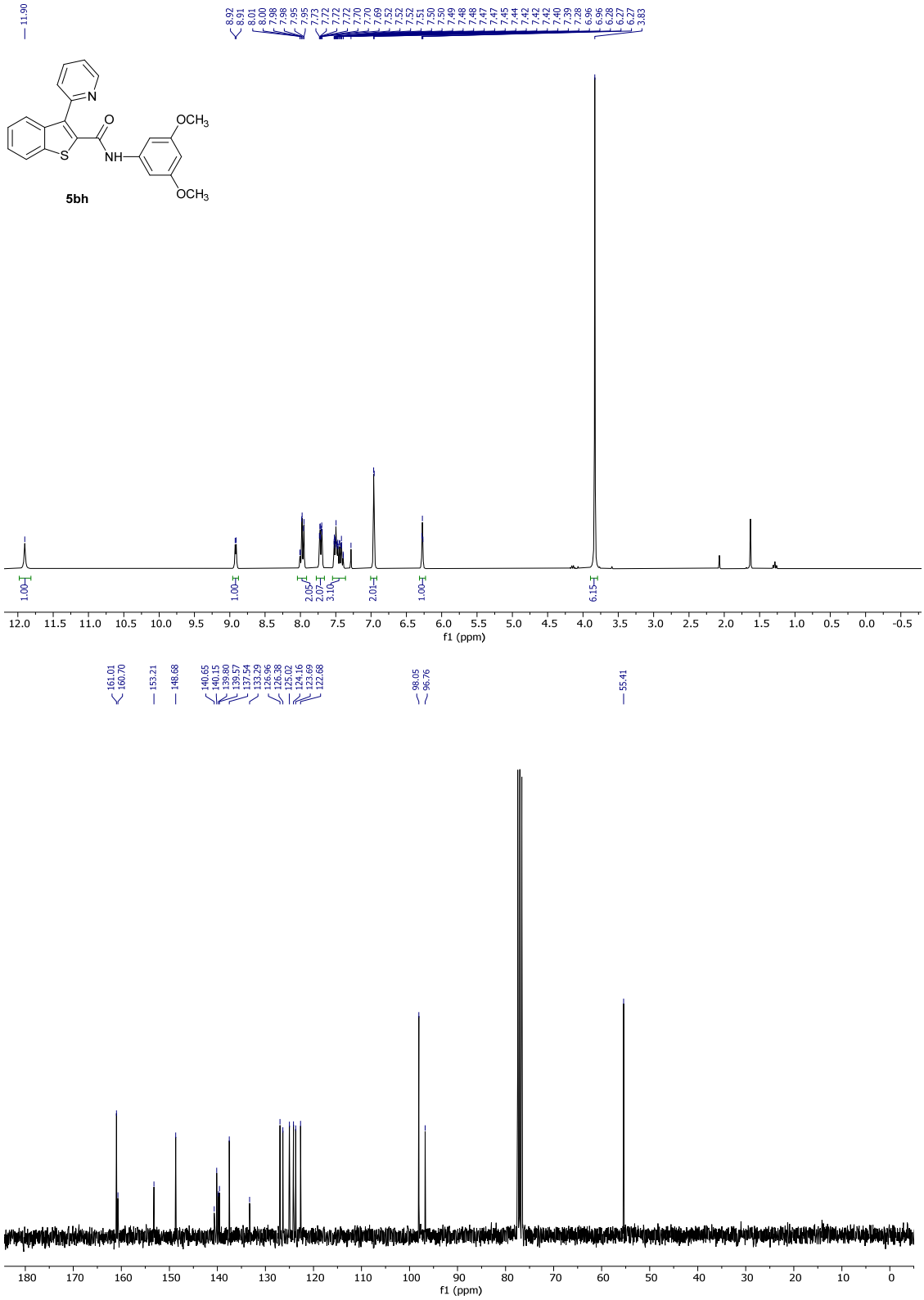


^{1}H and ^{13}C{^{1}H}-NMR spectra of **5bf**

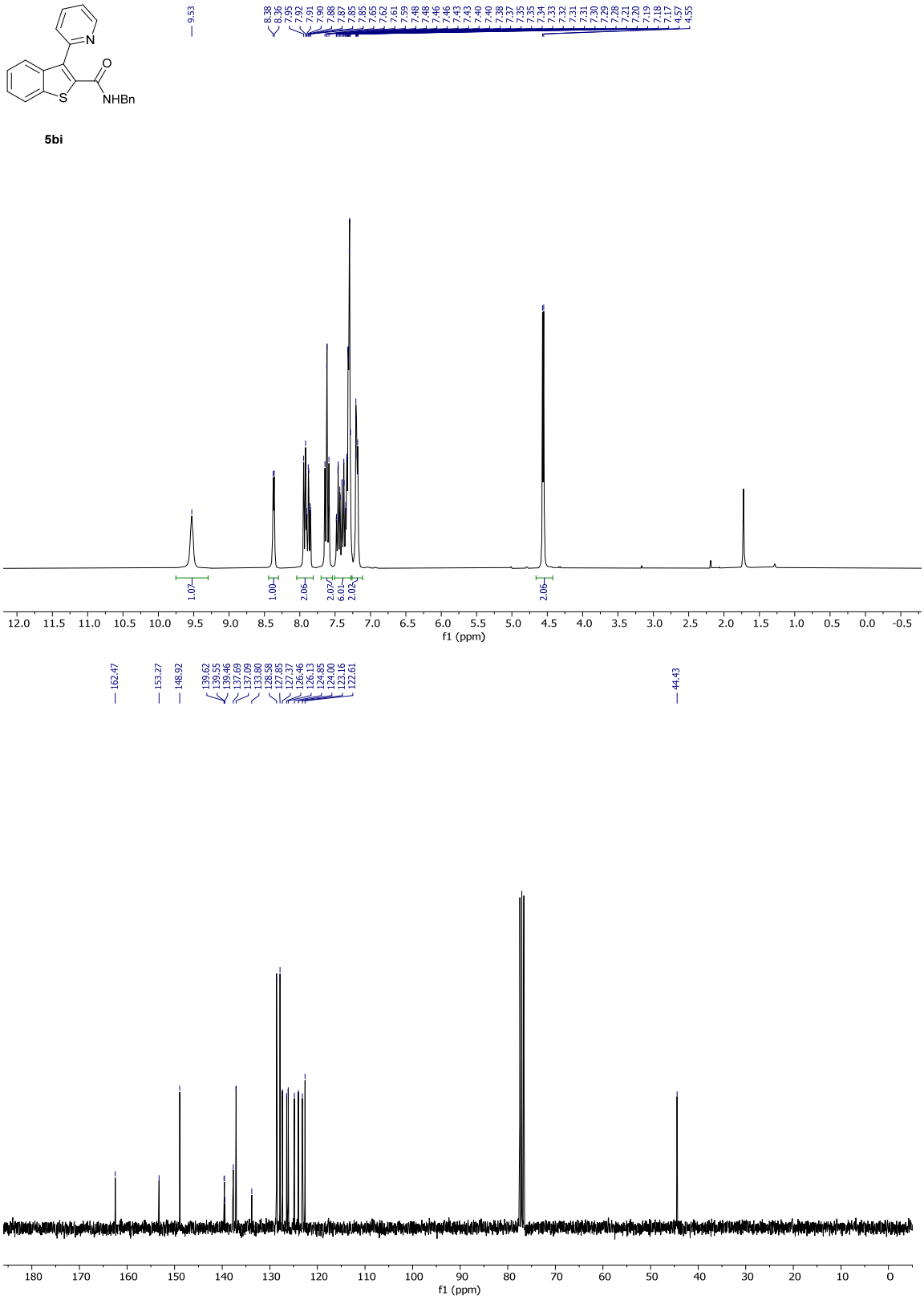




^{1}H and $^{13}C\{^{1}H\}$-NMR spectra of **5bg**

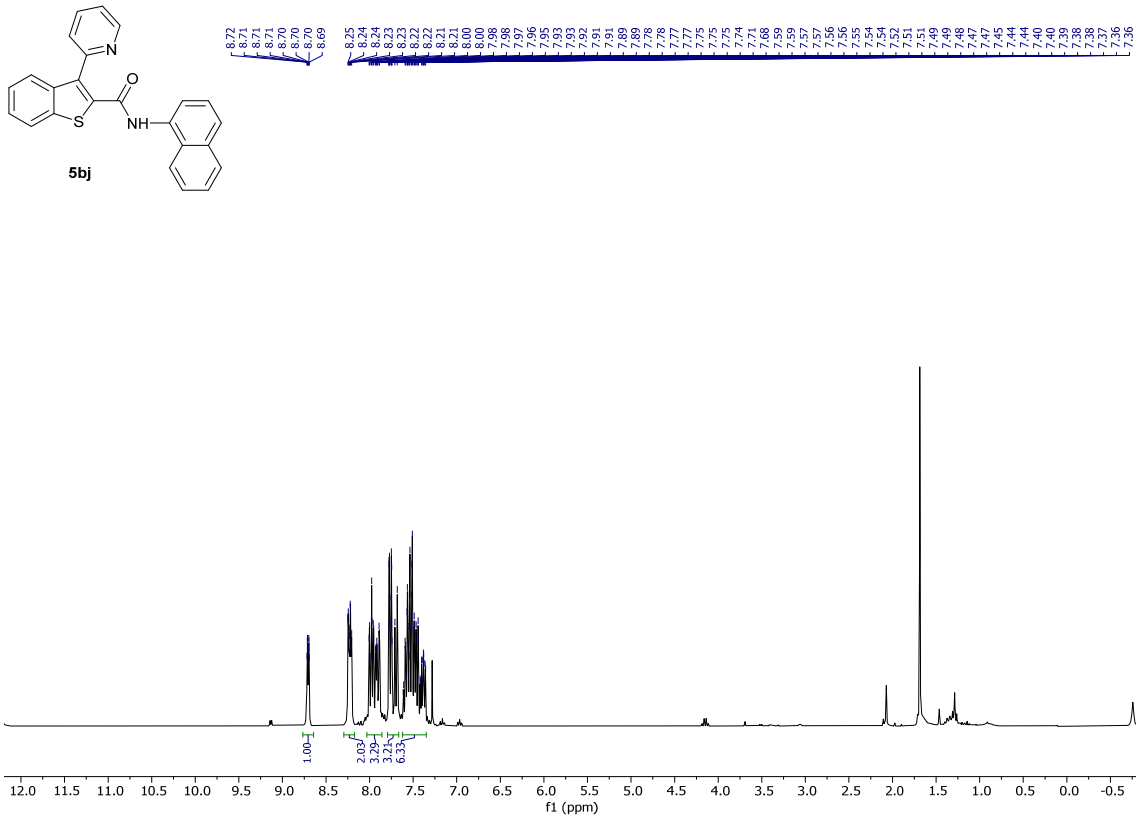


^{1}H and ^{13}C{^{1}H}-NMR spectra of **5bh**

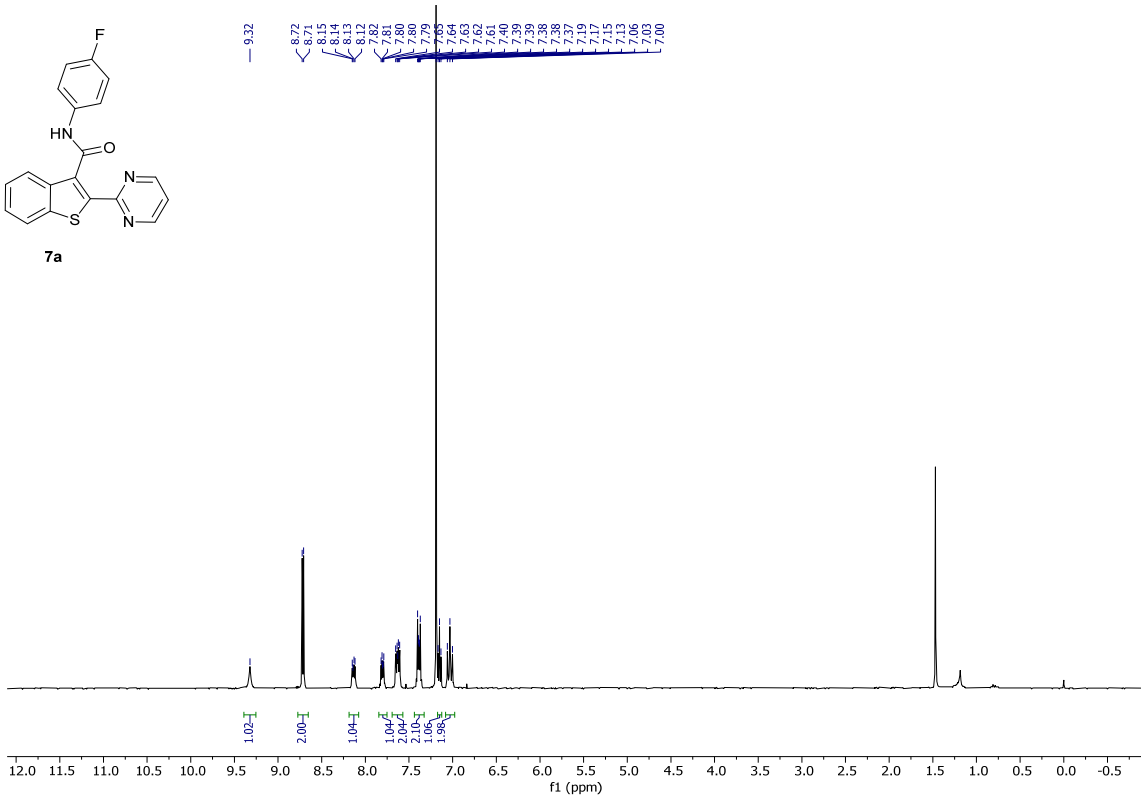


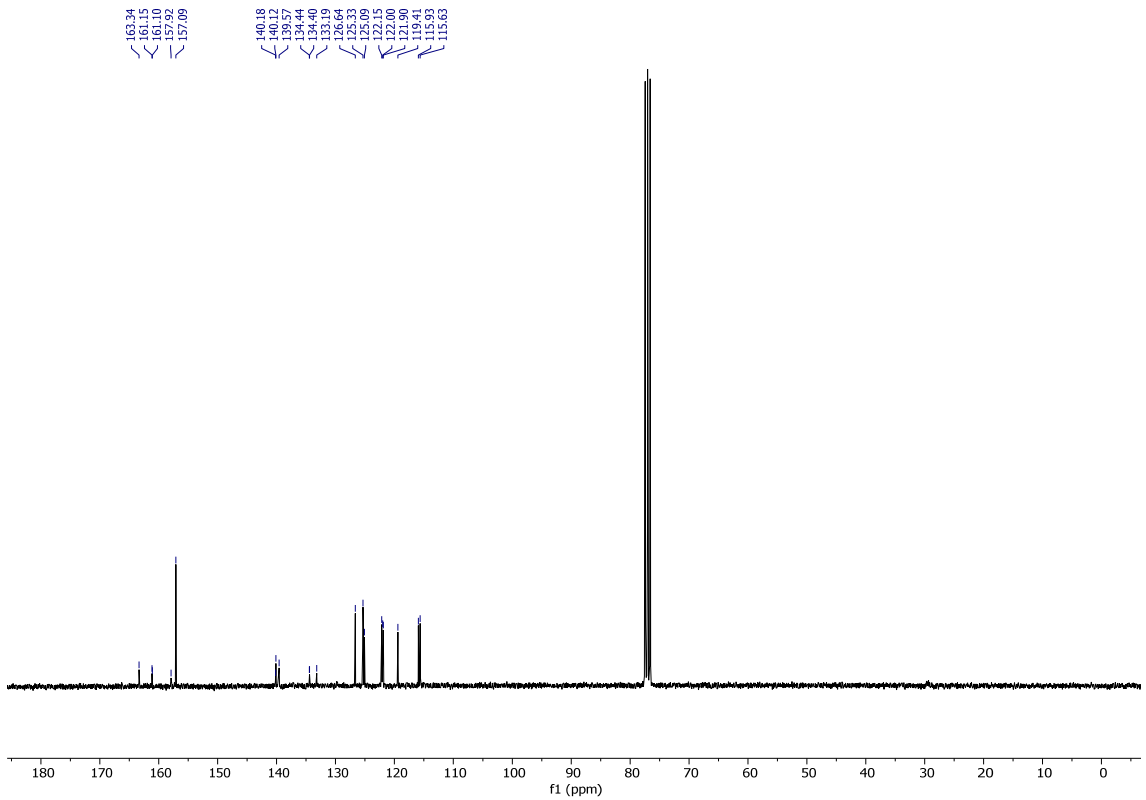
5bi

^{1}H and ^{13}C{^{1}H}-NMR spectra of **5bi**

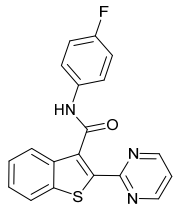


^{1}H and $^{13}C\{^{1}H\}$-NMR spectra of **5bj**

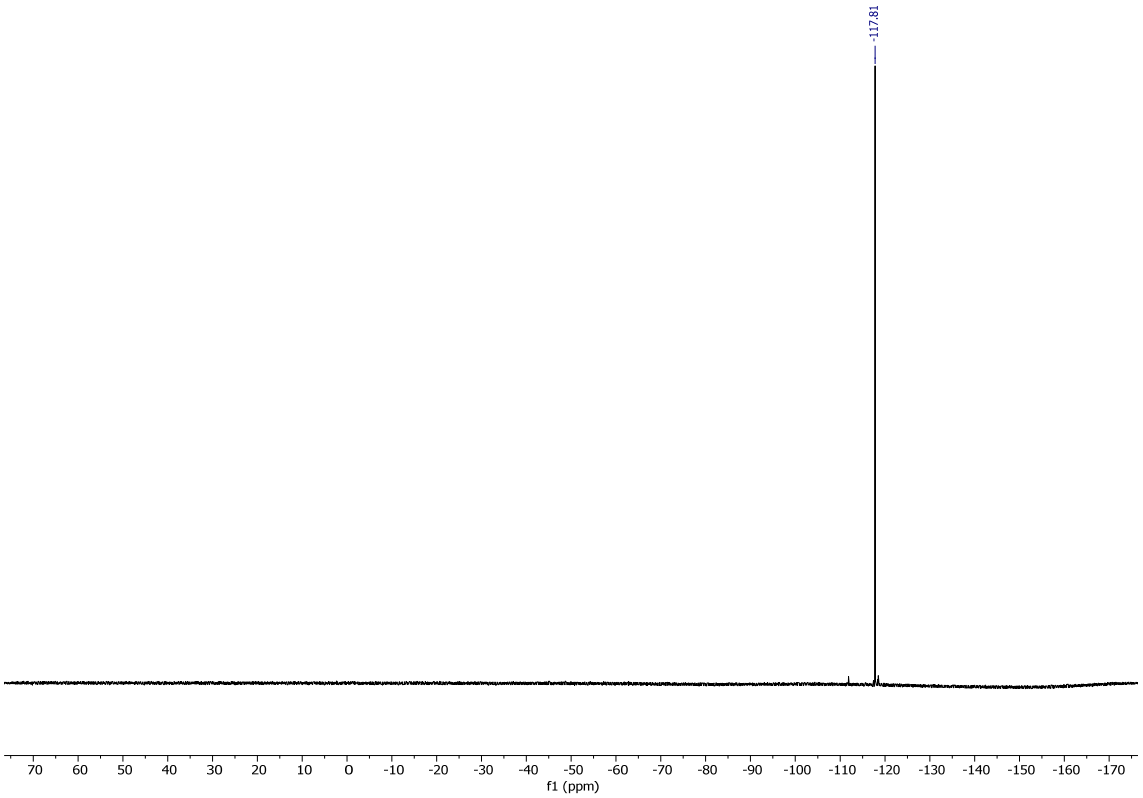




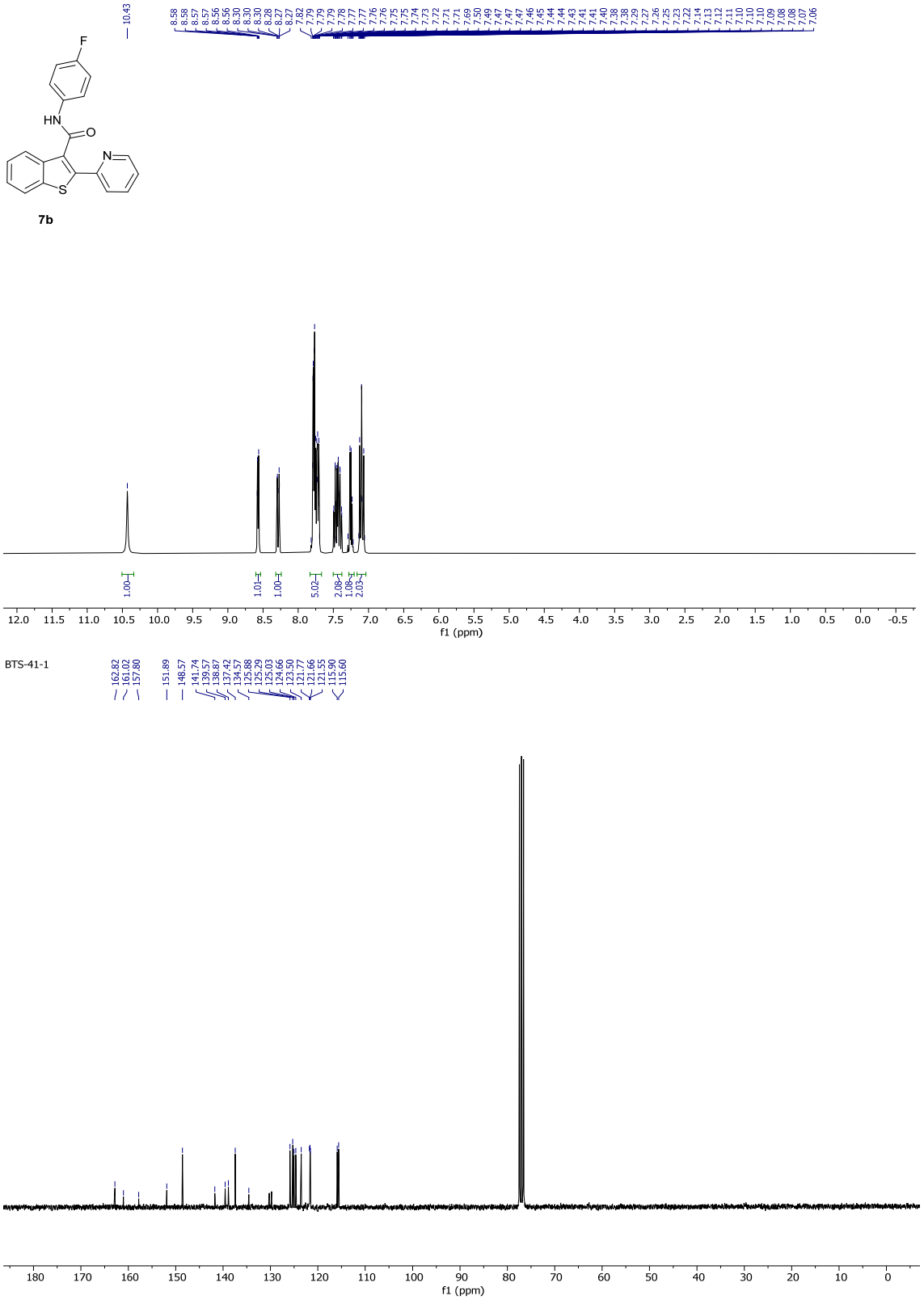
^{1}H and ^{13}C{^{1}H}-NMR spectra of **7a**



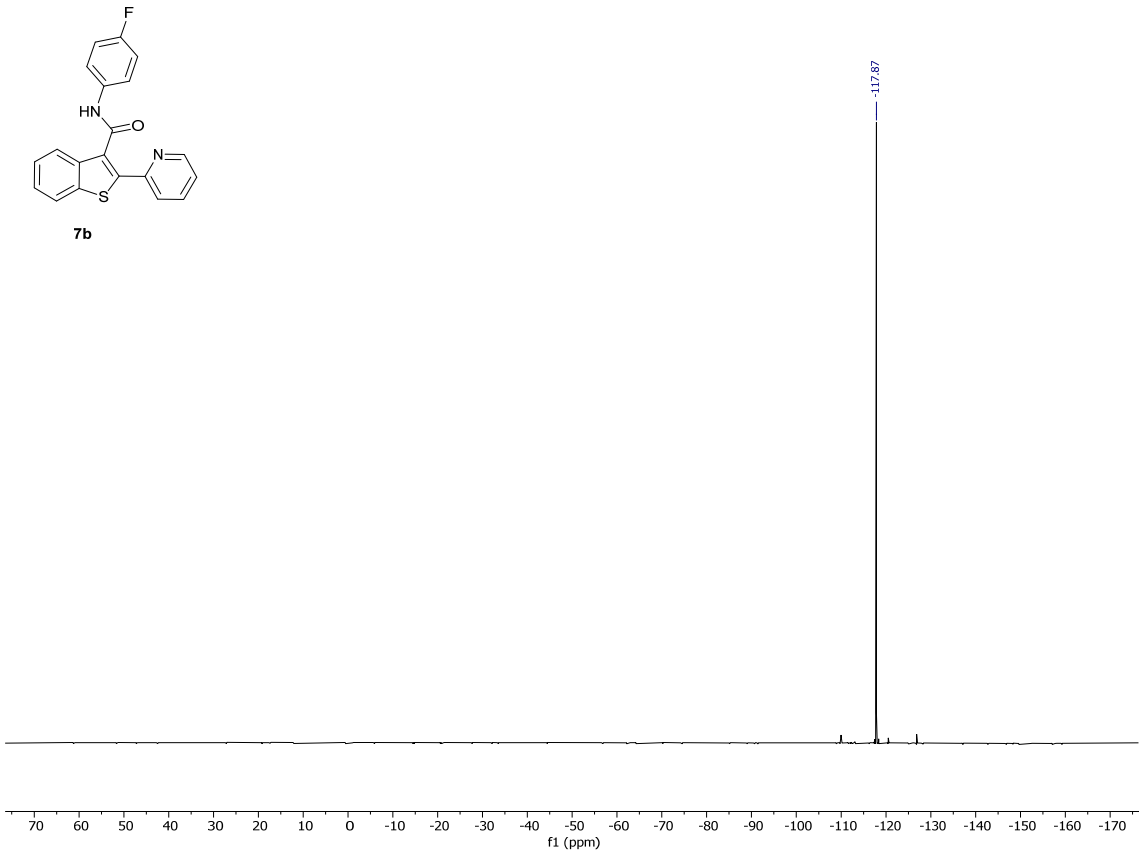
7a



^{19}F NMR spectrum of **7a**

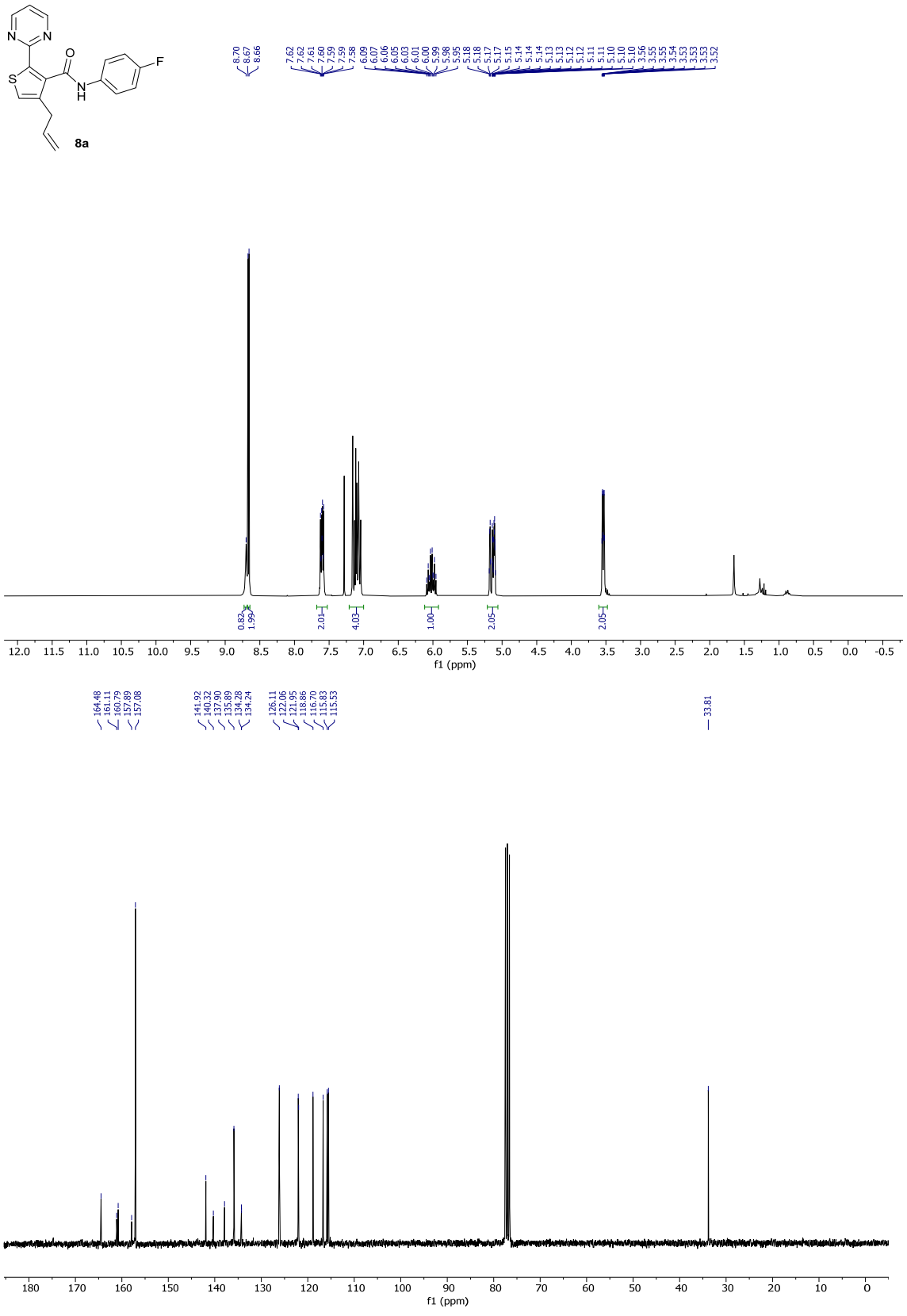


^{1}H and $^{13}C\{^{1}H\}$-NMR spectra of **7b**

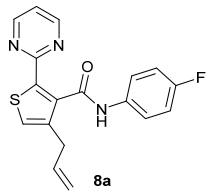


7b

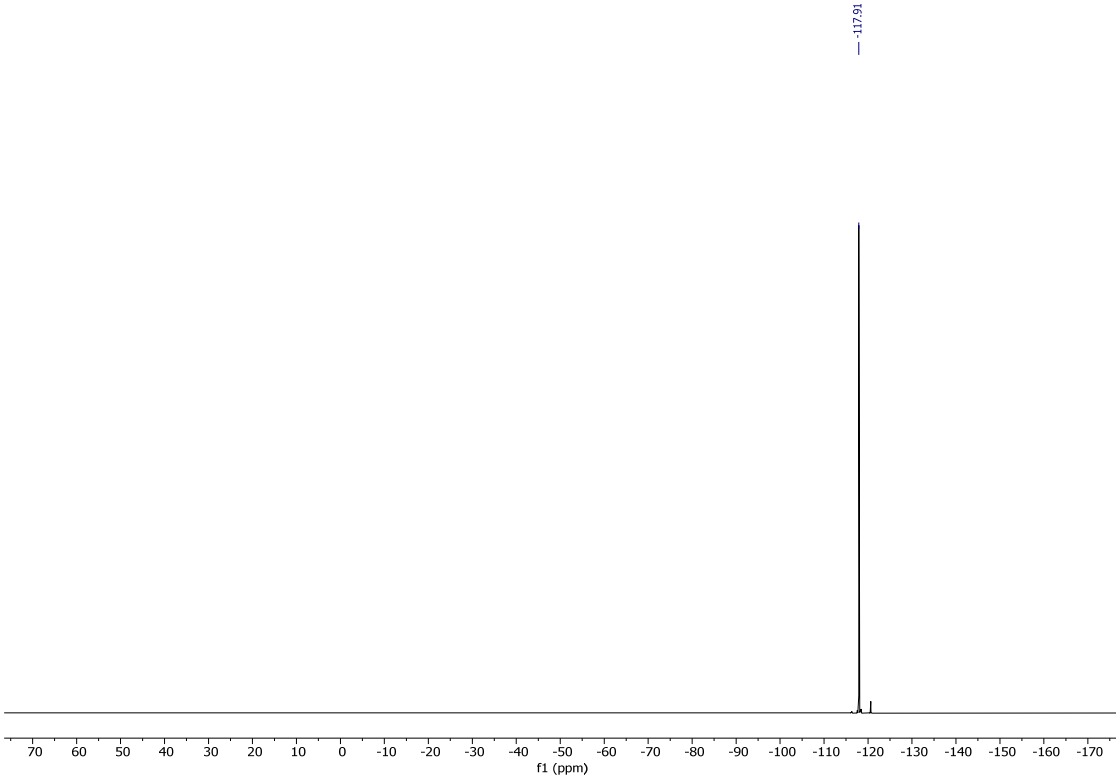
^{19}F NMR spectrum of **7b**



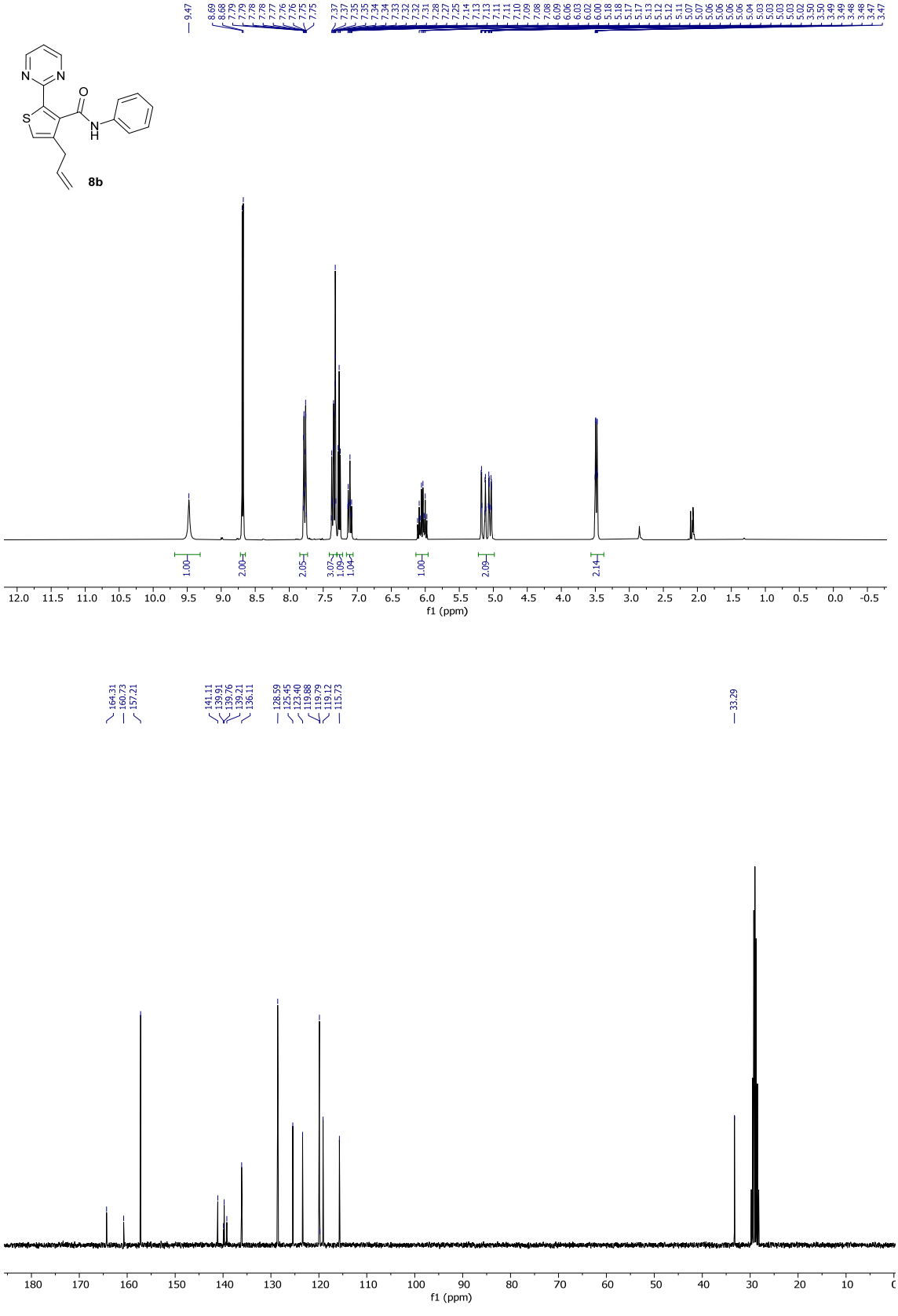
^{1}H and $^{13}C\{^{1}H\}$-NMR spectra of **8a**



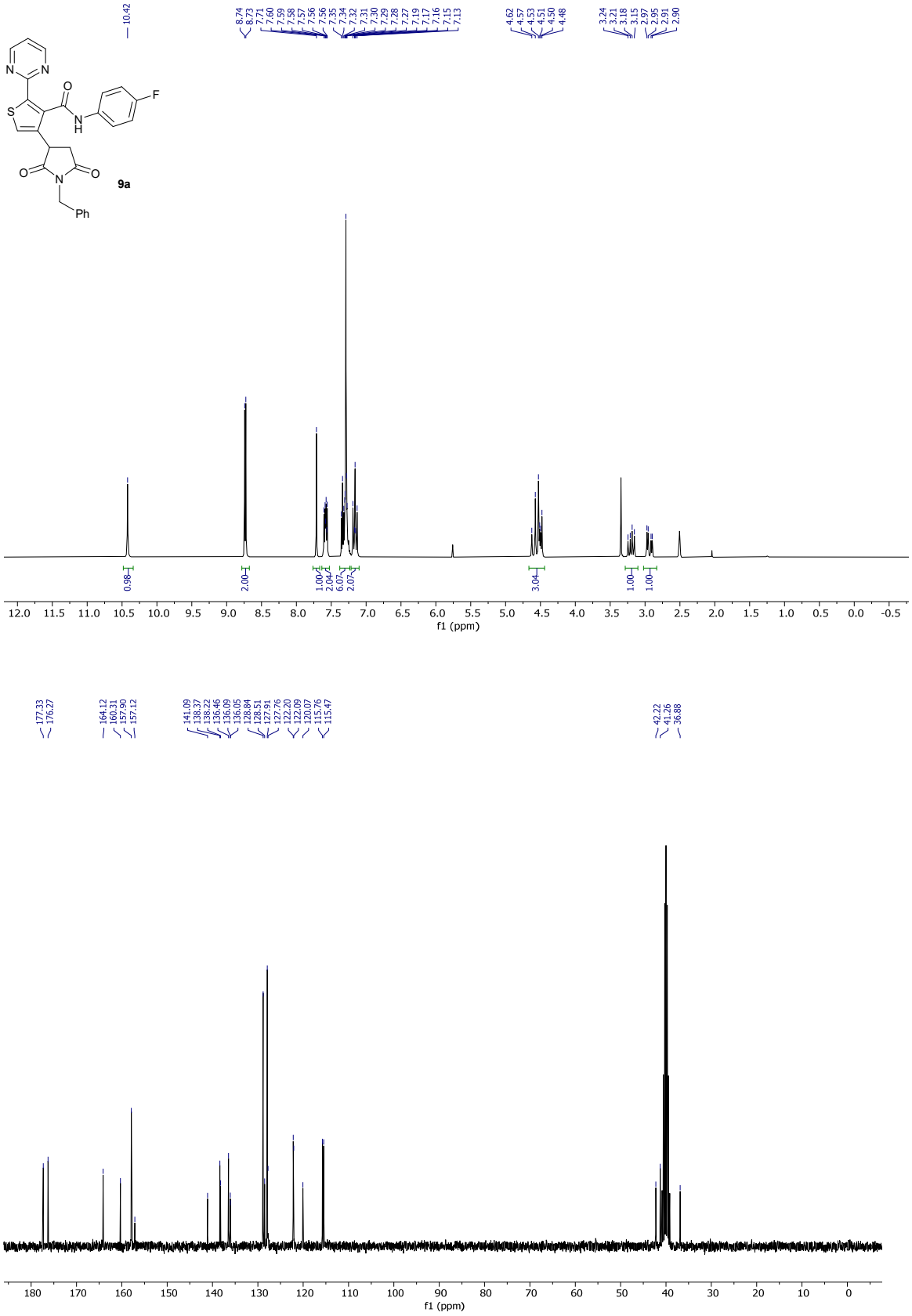
8a



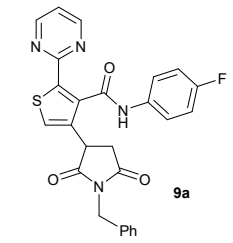
^{19}F NMR spectrum of **7b**



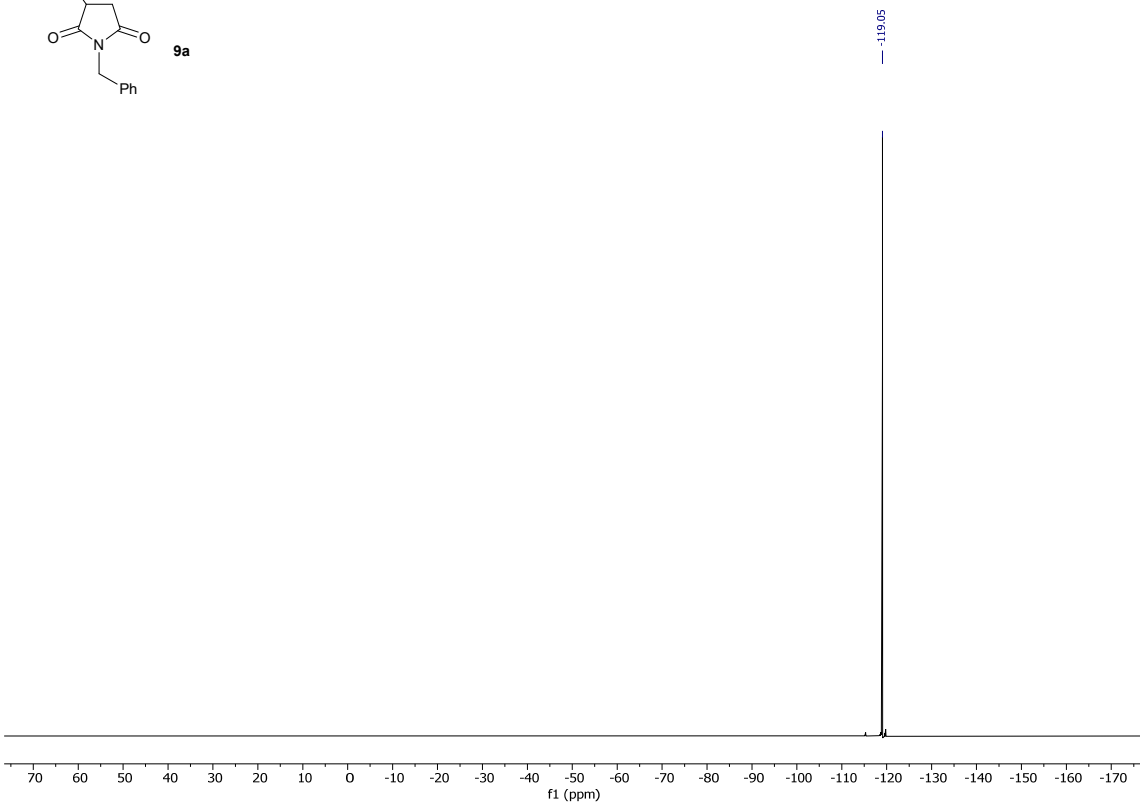
^{1}H and ^{13}C{^{1}H}-NMR spectra of **8b**



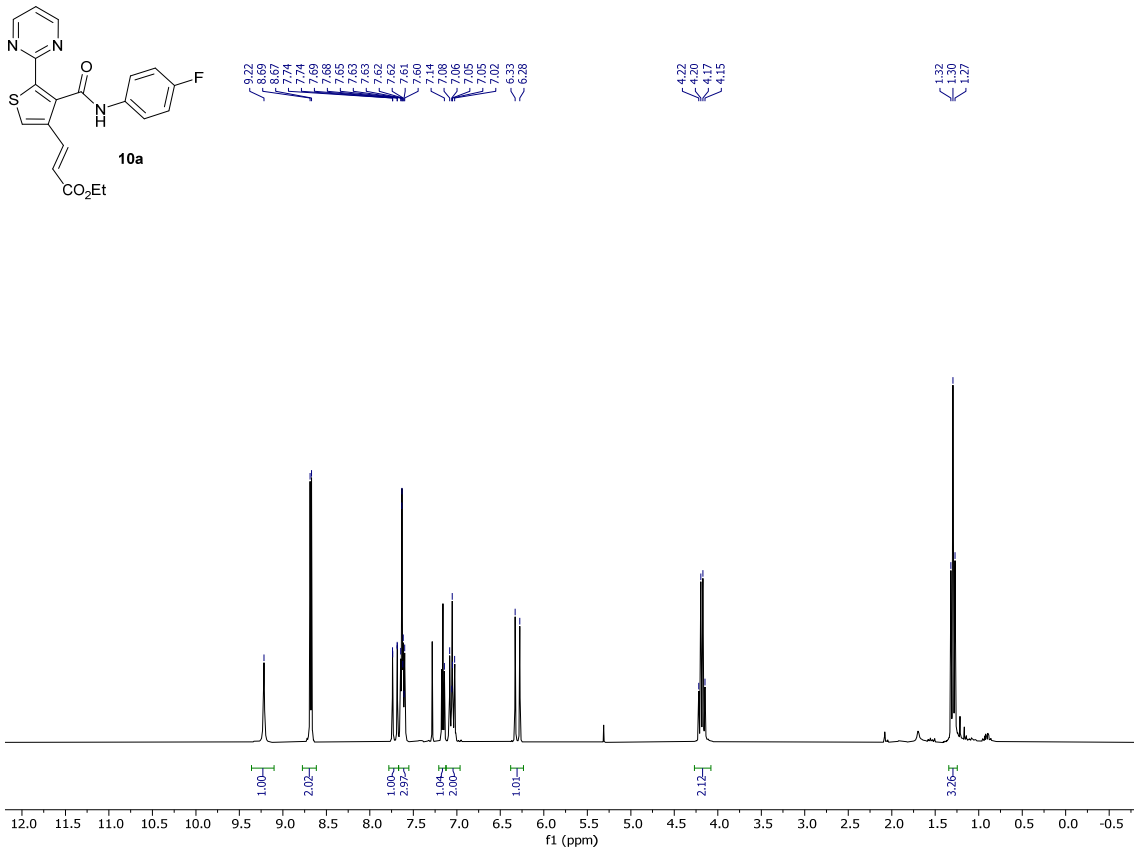
^{1}H and ^{13}C{^{1}H}-NMR spectra of **9a**

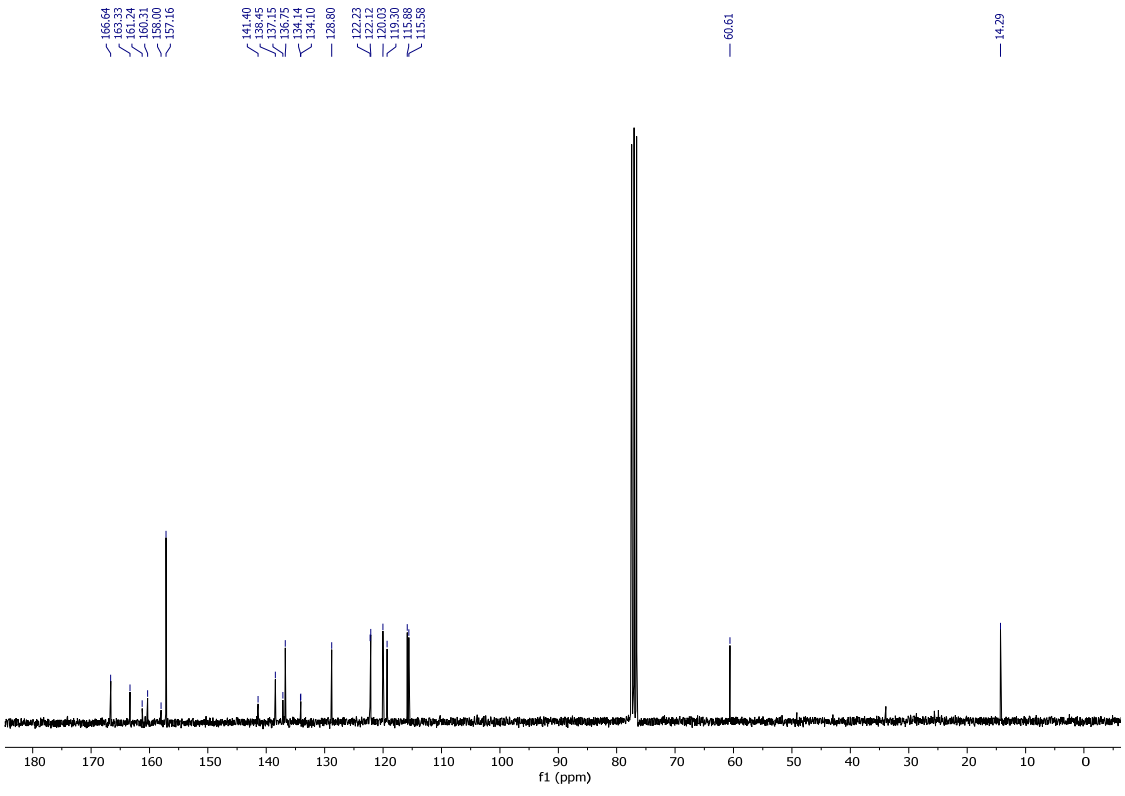


9a

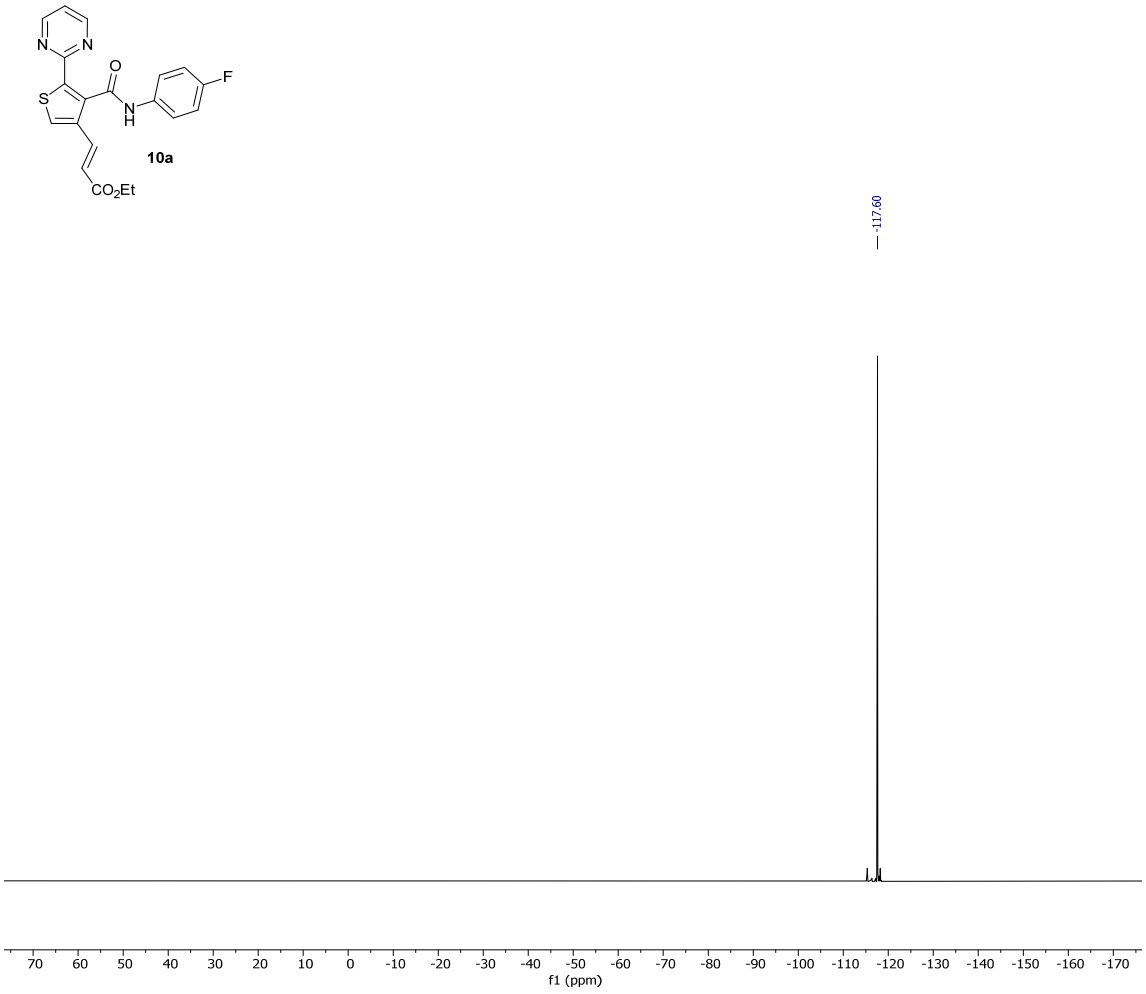


^{19}F NMR spectrum of **9a**





^{1}H and ^{13}C{^{1}H}-NMR spectra of **10a**



^{19}F NMR spectrum of **10a**