Supporting Information

Visible-light driven electron-donor-acceptor (EDA) complex initiated synthesis of thio-functionalized pyridines

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Contents:

1. General Information:

All the reagents were commercial grade and purified according to the established procedures. All the reactions were carried out in oven-dried glassware. The highest commercial quality reagents were purchased and were used without further purification unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) on 0.25 mm silica gel plates ($60F_{254}$) visualized under UV illumination at 254 nm. Organic extracts were dried over anhydrous sodium sulfate (Na_2SO_4). Solvents were removed using a rotary evaporator under reduced pressure. Column chromatography was performed to purify the crude product on silica gel 60–120 mesh using a mixture of hexane and ethyl acetate as eluent. The isolated compounds were characterized by spectroscopic [^{1}H, ^{13}C{1H} NMR, and IR] techniques and HRMS analysis. NMR spectra were recorded in deuterochloroform ($CDCl_3$). ^{1}H, ^{13}C{^{1}H} were recorded in 500 (125) or 400 (100) MHz spectrometer and were calibrated using tetramethylsilane or residual undeuterated solvent for ^{1}H NMR, deuterochloroform for ^{13}C NMR as an internal reference {$Si(CH_3)_4$: 0.00 ppm or $CHCl_3$: 7.260 ppm for ^{1}H NMR, 77.230 ppm for ^{13}C NMR}. ^{19}F NMR was calibrated without any internal standard in $CDCl_3$ and DMSO-d_6 in a 500 MHz spectrometer. The chemical shifts are quoted in δ units, parts per million (ppm). ^{1}H NMR data is represented as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration and coupling constant(s) *J* in hertz (Hz). High-resolution mass spectra (HRMS) were recorded on a mass spectrometer using electrospray ionization-time of flight (ESI-TOF) reflection experiments. FT-IR spectra were recorded in KBr or neat and reported in the frequency of absorption (cm^{-1}). All UV experiments were performed in 3 mL quartz cuvettes of path length 1 cm at 25 ^{o}C in UV/Vis spectrometer in HPLC grade toluene.

2. Light Information and Reaction Setup:

Philips 2 x 14 W white LED (flux 46 mW/cm^2) bulbs were used as the light source for this light-promoted reaction and no filter was used. A borosilicate 10 mL vial was used as the reaction vessel. The distance from the light source to the irradiation vessel was ~6–8 cm. Regular fan was used to ventilate the area to maintain the room temperature (27–30 ^{o}C). The reaction set-up for this photochemical reaction is shown below (Figure S1).

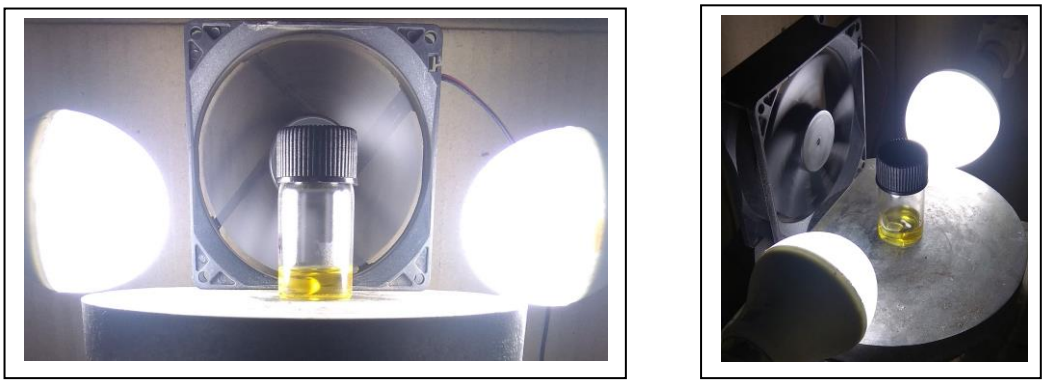


Figure S1. Photochemical Reaction Set-up

3. Representative Drugs Containing Pyridines

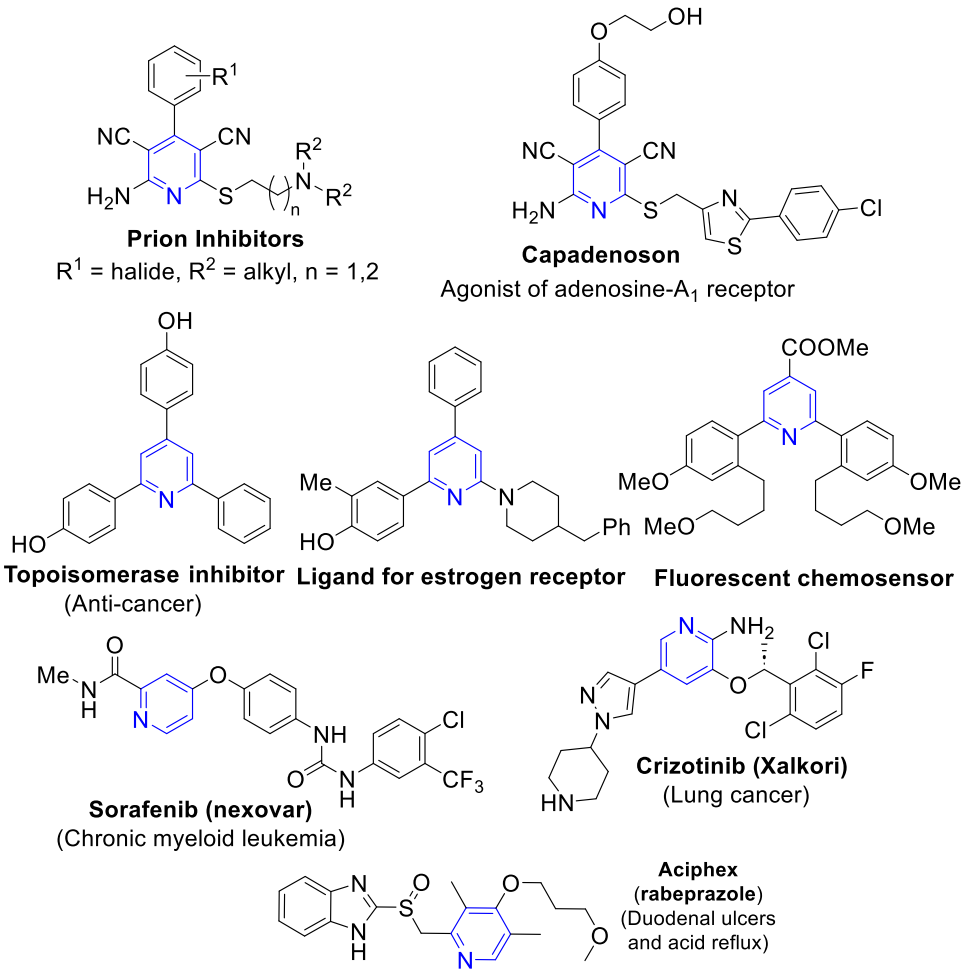


Figure S2. Pyridine Containing Drugs

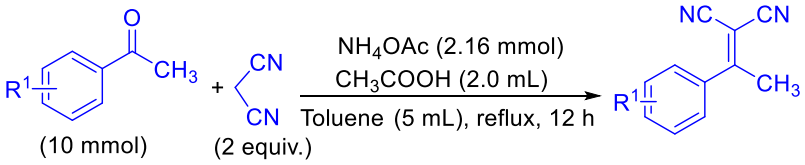
4. General Procedure:

(A) General Procedure for the Synthesis of (*E*)-2-(1,3-Diarylallylidene)malononitriles (1–21):

Compounds **1**–**21** were synthesized in slightly modified literature procedures[1]

(i) General Procedure for the Synthesis of 2-(1-Phenylethylidene)malononitrile:

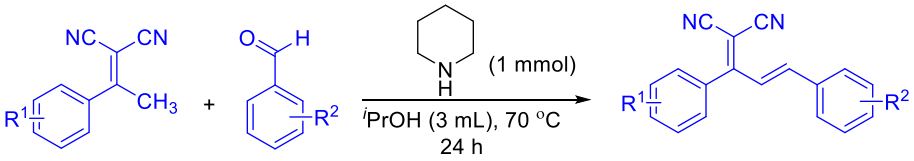
To an oven-dried 50 mL round bottom flask fitted with a reflux condenser was added acetophenone (1.20 g, 10 mmol), malononitrile (1.30 g, 20 mmol), and ammonium acetate (0.164 g, 2.16 mmol) in 5 mL of toluene and glacial acetic acid (2.0 mL). The reaction mixture was refluxed vigorously in a preheated oil bath for 12 h. The progress of the reaction was monitored by TLC. After completion of the reaction the mixture was cooled to room temperature, admixed with ethyl acetate (50 mL), and the organic layer was washed with saturated bicarbonate solution (20 mL). The organic layer was dried over anhydrous sodium sulfate (Na_2SO_4), and the solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel using hexane/ethyl acetate = 98:2 to give pure 2-(1-phenylethylidene)malononitrile (1.35 g, 80%) (Scheme S1).



Scheme S1. **Synthesis of 2-(1-Arylethylidene)malononitriles.**

(ii) General Procedure for the Synthesis of (*E*)-2-(1,3-Diphenylallylidene)malononitrile:

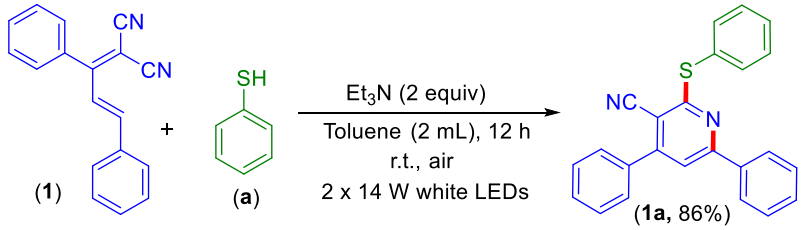
To an oven-dried 50 mL round bottom flask was added 2-(1-phenylethylidene)malononitrile (1.68 g, 10 mmol), benzaldehyde (1.06 g, 10 mmol), and piperidine (0.085 g/98 µL, 1 mmol,) in ^{i}PrOH (3 mL). The reaction mixture was stirred at 70 ^{o}C in a preheated oil bath for 24 h. Completion of the reaction was monitored by TLC. Then the reaction mixture was cooled to room temperature, admixed with ethyl acetate (50 mL) and the organic layer was washed with brine (20 mL). The organic layer was dried over anhydrous sodium sulfate (Na_2SO_4), and the solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel using hexane/ethyl acetate = 99:1 to give pure (*E*)-2-(1,3-diphenylallylidene)malononitrile in (1.56 g) 60% yield. (Scheme S2).



Scheme S2. Synthesis of (*E*)-2-(1,3-Diarylallylidene)malononitriles (1–21).

(B) (i) General Procedure for the Synthesis of 4,6-Diphenyl-2-(phenylthio)nicotinonitrile (1a) from (*E*)-2-(1,3-Diphenylallylidene)malononitrile (1) and Thiophenol (a):

To an oven-dried 10 mL vial was added (*E*)-2-(1,3-diphenylallylidene)malononitrile (**1**) (0.0640 g, 0.25 mmol), thiophenol (**a**) (0.082 g/76 µL, 0.75 mmol), and Et_3N (0.050 g/70 µL, 0.5 mmol) in toluene (2 mL) in air atmosphere. The reaction mixture was stirred at room temperature for 12 h, maintaining an approximate distance of ~6–8 cm from two 14 W white LED bulbs. After completion of the reaction (monitored by TLC analysis), the reaction mixture was admixed with ethyl acetate (20 mL) and the organic layer was washed with water (20 mL). The organic layer was dried over anhydrous sodium sulfate (Na_2SO_4), and the solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel using 2% ethyl acetate in hexane to give pure 4,6-diphenyl-2-(phenylthio)nicotinonitrile (**1a**) in 86% yield (78 mg) (Scheme S3). The identity and purity of the product were confirmed by spectroscopic analysis.

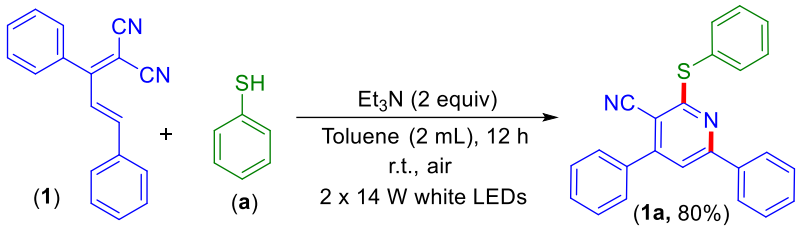


Scheme S3. Synthesis of 4,6-diphenyl-2-(phenylthio)nicotinonitrile (1a)

(ii) Gram-scale Synthesis of 4,6-Diphenyl-2-(phenylthio)nicotinonitrile (1a) from (*E*)-2-(1,3-Diphenylallylidene)malononitrile (1) and Thiophenol (a):

To an oven-dried 50 mL round bottom flask was added (*E*)-2-(1,3-diphenylallylidene)malononitrile (**1**) (1.28 g, 5.0 mmol), thiophenol (**a**) (1.65 g/1.2 mL, 15.0 mmol,), and Et_3N (1.01 g/1.04 mL, 10.0 mmol,) in toluene (5 mL) in air atmosphere. The reaction mixture was stirred at room temperature for 12 h, maintaining an approximate distance of ~6–8 cm from two 14 W white LED bulbs. After completion of the reaction (monitored by TLC

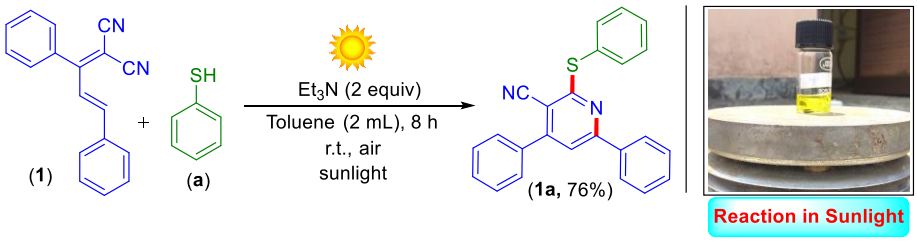
analysis), the reaction mixture was admixed with ethyl acetate (50 mL) and the organic layer was washed with water (2 x 20 mL). The organic layer was dried over anhydrous sodium sulfate (Na_2SO_4), and the solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel using 2% ethyl acetate in hexane to give pure 4,6-diphenyl-2-(phenylthio)nicotinonitrile (**1a**) in 80% yield (1.46 g) (Scheme S4). The identity and purity of the product were confirmed by spectroscopic analysis.



Scheme S4. Gram-scale synthesis of 4,6-diphenyl-2-(phenylthio)nicotinonitrile (1a)

(ii) General Procedure for the Synthesis of 4,6-Diphenyl-2-(phenylthio)nicotinonitrile (1a) in the Presence of Sunlight:

To an oven-dried 10 mL vial was added (*E*)-2-(1,3-diphenylallylidene)malononitrile (**1**) (0.0640 g, 0.25 mmol), thiophenol (**a**) (0.082 g/76 µL, 0.75 mmol), and Et_3N (0.050 g/70 µL, 0.5 mmol) in toluene (2 mL) in air atmosphere. The reaction mixture was stirred under sunlight with a surrounding temperature was 28-35 ^oC for 8 h. After completion of the reaction (monitored by TLC analysis), the reaction mixture was admixed with ethyl acetate (20 mL), and the organic layer was washed with water (20 mL). The organic layer was dried over anhydrous sodium sulfate (Na_2SO_4), and the solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel using 2% ethyl acetate in hexane to give pure 4,6-diphenyl-2-(phenylthio)nicotinonitrile (**1a**) in 76% yield (69 mg) (Scheme S5). The identity and purity of the product were confirmed by spectroscopic analysis.

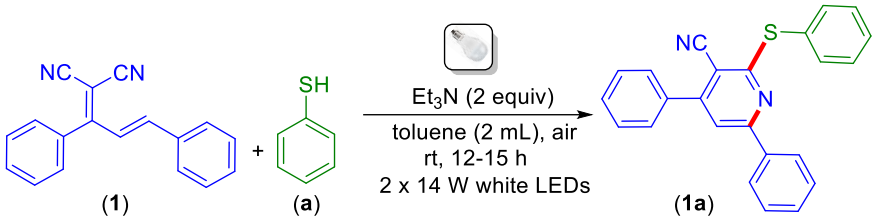


Scheme S5. Synthesis of 4,6-diphenyl-2-(phenylthio)nicotinonitrile (1a) in sunlight

5. Optimization of the Reaction:

Initially, we selected (*E*)-2-(1,3-diphenylallylidene)malononitrile (**1**) and thiophenol (**a**) as the model substrates to explore the optimal reaction conditions for the formation of 4,6-diphenyl-2-(phenylthio)nicotinonitrile (**1a**) (Table S1). To our delight, when a mixture of **1** (0.25 mmol), **a** (0.75 mmol, 76 μL), and Et_3N (2.0 equiv, 0.5 mmol, 70 μL) in toluene (2 mL) was irradiated with visible light [2 x 14 W white LEDs (flux 46 mW/cm^2)] at room temperature for12 h, it delivers the desired product **1a** in 86% isolated yield (Table S1, entry 1). The use of other solvents such as 1,2-dichloroethane (DCE) (65%), CH_3CN (27%), 2,2,2-trifluoroethanol (TFE) (53%), MeOH (63%), and DMSO (52%) resulted in lower yields (Table S1, entry 2). The reaction with inorganic bases *viz.* K_2CO_3 (trace), and KOAc (00%) didn't give the product whereas organic bases such as DBU (50%), DABCO (62%), and DIPEA (81%) failed to improve the yield (Table S1, entry 3). Inorganic bases such as K_2CO_3 and KOAc being ionic in nature are insoluble in non-polar solvents such as toluene. Thus, the reaction medium is non-homogeneous and sufficiently basic to be able to deprotonate thiophenol to generate a thiophenolate anion which is necessary for the formation of the EDA complex. Next to confirm the role of the base this reaction was carried out in the absence of Et_3N (Table S1, entry 4). A sharp decrease in the yield (10%), suggested base is indispensable for this protocol. Further, no improvement in the yield (83%) was observed when the reaction was carried out with an increasing amount (3 equiv) of Et_3N (Table S1, entry 5). Next, to investigate the role of air (O_2) a reaction was carried out under a nitrogen atmosphere (Table S1, entry 6). The yield (13%) of product **1a** drops sharply, indicating that air (O_2) was critical for this cyclization. The reaction was also carried out under O_2 atmosphere which gave 87% yield of the product, suggesting an essential role of O_2 (Table S1, entry 7). Further, the reaction in the absence of light produces **1a** with a very low yield (16%), suggesting the essential role of light in this transformation (Table S1, entry 8). The reaction was also tested with light sources of different wavelengths such as green LEDs (513 nm) and blue LEDs (432 nm). Unfortunately, both light sources failed to improve the yield of **1a** (Table S1, entry 9). So, the best-optimized conditions for this protocol was found to be the use of (*E*)-2-(1,3-diphenylallylidene)malononitrile (**1**, 0.25 mmol) and thiophenol (**a**, 0.75 mmol, 76 μL), Et_3N (0.5 mmol, 70 μL) in toluene (2 mL) in the presence of an aerial atmosphere at room temperature for 12 h

Table S1. Optimization of the reaction conditions



Entry	Variation from the standard condition	% yield of **1a**
1	None	86
2	DCE, CH_3CN, TFE, MeOH, DMSO instead of toluene	65, 27, 53, 63, 52
3	K_2CO_3, KOAc, DBU, DABCO, DIPEA instead of Et_3N	trace, 00, 50, 62, 81
4	Without Et_3N	10
5	3 equiv of Et_3N instead of 2 equiv of Et_3N	83
6	N_2 instead of air	13
7	O_2 instead of air	87
8	Without light	16
9	Green LEDs, blue LEDs instead of white LEDs	70, 67

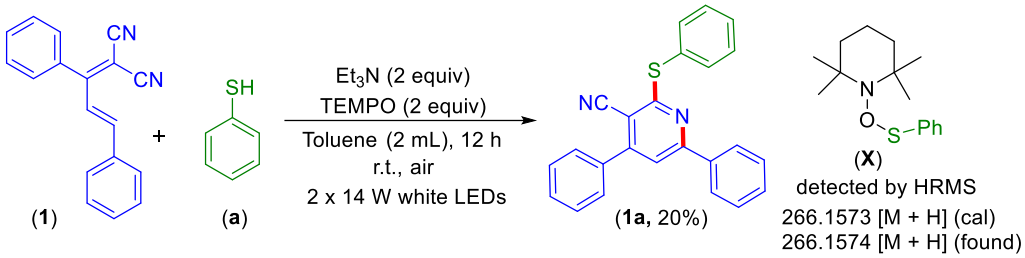
6. Mechanistic Investigation:

(A) Radical-trapping Experiments with TEMPO:

(i) Reaction in the Presence of 2 equiv of TEMPO:

To an oven-dried 10 mL vial was added (*E*)-2-(1,3-diphenylylallylidene)malononitrile (**1**) (0.064g, 0.25 mmol), thiophenol (**a**) (0.0825 g/76 µL, 0.75 mmol), Et_3N (0.0505 g/70 µL, 0.5 mmol,), and (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) (0.078 g, 0.5 mmol) in toluene (2 mL). The reaction mixture was stirred at room temperature for 12 h maintaining an approximate distance of ~6-8 cm from two 14 W white LED bulbs. After completion of the reaction (monitored by TLC analysis), the reaction mixture was admixed with ethyl acetate (25 mL) and the organic layer was washed with water (20 mL). The organic layer was dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel using 2% ethyl acetate in hexane to give pure 4,6-diphenyl-2-(phenylthio)nicotinonitrile (**1a**) (18 mg, 20% yield) (Scheme S6). The identity and purity of the product were confirmed by spectroscopic analysis.

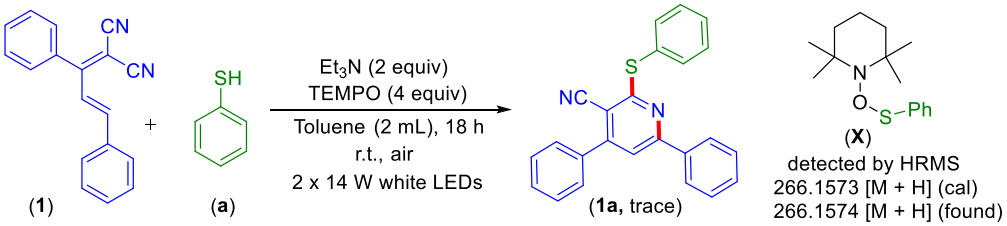
In another set of identical reactions formation of TEMPO-thiol adduct was monitored. Each time (10 μL) of reaction aliquot was taken at a time interval of 20 minutes and subjected to HRMS analysis. A TEMPO-thiophenol adduct (**X**) was detected after 1 h (Figure S3, page S10).



Scheme S6. Reaction in the presence of 2 equiv of TEMPO.

(B) Reaction in the Presence of 4 equiv of TEMPO:

To an oven-dried 10 mL vial was added (*E*)-2-(1,3-diphenylylallylidene)malononitrile (**1**) (0.064g, 0.25 mmol), thiophenol (**a**) (0.0825 g/76 μL, 0.75 mmol), Et_3N (0.0505 g/70 μL, 0.5 mmol), and (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) (0.156 g, 1.0 mmol) in toluene (2 mL). The reaction mixture was stirred at room temperature for 15 h maintaining an approximate distance of ~6-8 cm from two 14 W white LED bulbs. After 18 h of the reaction (monitored by TLC analysis), it was found that a trace amount of product 4,6-diphenyl-2-(phenylthio)nicotinonitrile (**1a**) was formed (Scheme S7). The result suggests that the reaction goes through a radical pathway. However, the TEMPO-thiophenol adduct (**X**) cannot be isolated by column chromatography but it is detected from the HRMS analysis of the reaction mixture (Figure S3).



Scheme S7. Reaction in the presence of 4 equiv of TEMPO.

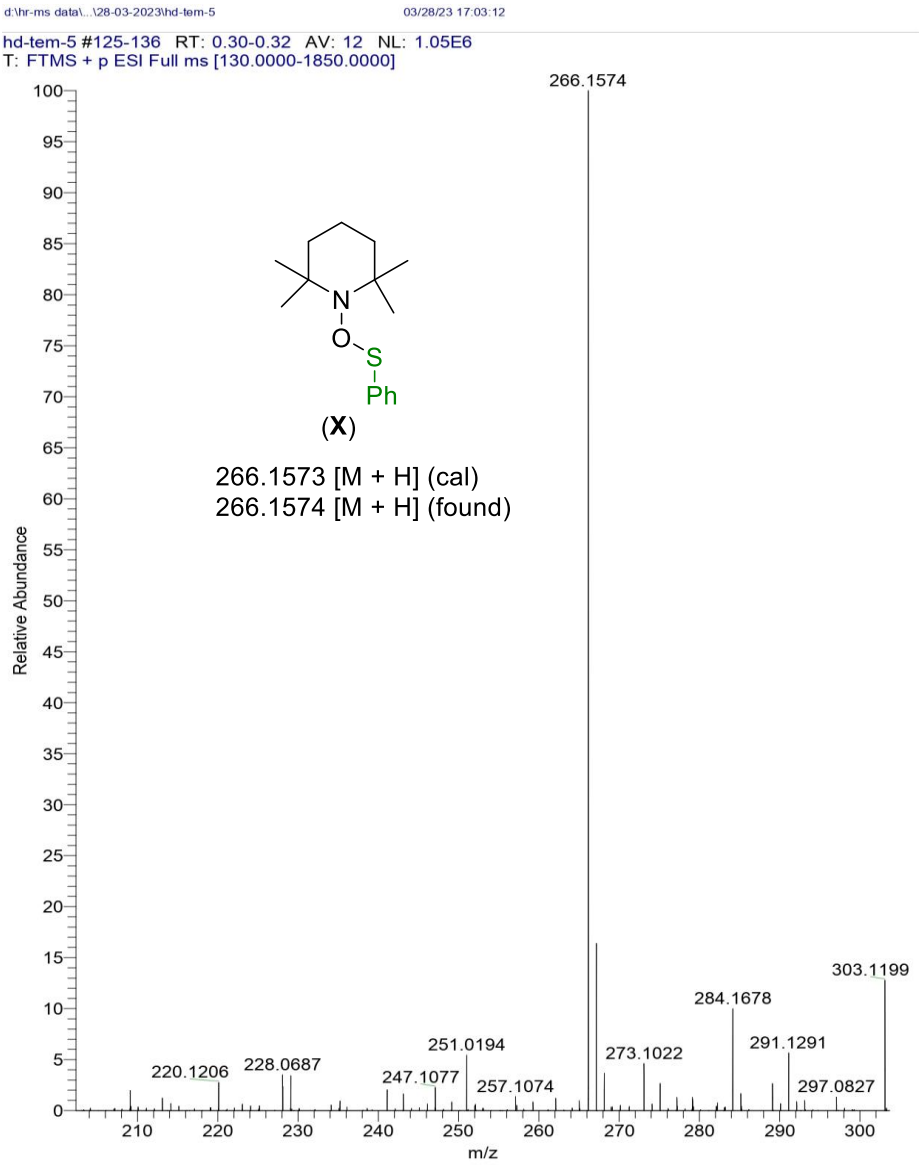
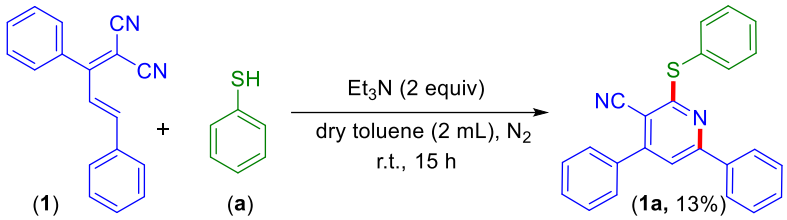


Figure S3: HRMS of TEMPO-thiophenol adduct (X)

(C) Reaction in the Presence of N_2 Atmosphere:

To an oven-dried 10 mL vial was added (*E*)-2-(1,3-diphenylallylidene)malononitrile (**1**) (0.0640 g, 0.25 mmol), thiophenol (**a**) (0.0825 g/76 μL, 0.75 mmol), and Et_3N (0.0505 g/70 μL, 0.5 mmol) in toluene (2 mL) in N_2 atmosphere. The reaction mixture was stirred at room temperature for 15 h, maintaining an approximate distance of ~6-8 cm from two 14 W white LED bulbs. After completion of the reaction (monitored by TLC analysis), the reaction mixture was admixed with ethyl acetate (25 mL) and the organic layer was washed with water (20 mL). The organic layer was dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel using 2% ethyl

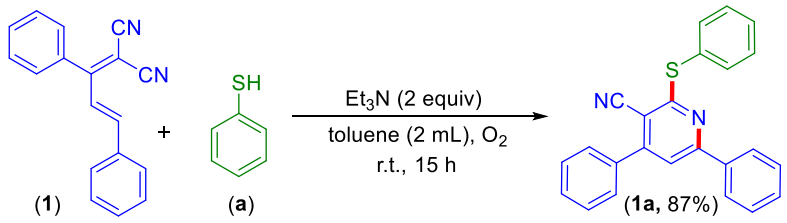
acetate in hexane to give pure 4,6-diphenyl-2-(phenylthio)nicotinonitrile (**1a**) (12 mg, 13%) (Scheme S8). The identity and purity of the product were confirmed by spectroscopic analysis.



Scheme S8. Reaction in presence of N_2 atmosphere

(D) Reaction in the Presence of O_2 Atmosphere:

To an oven-dried 10 mL vial was added (*E*)-2-(1,3-diphenylallylidene)malononitrile (**1**) (0.0640 g, 0.25 mmol), thiophenol (**a**) (0.0825 g/76 µL, 0.75 mmol), and Et_3N (0.0505 g/70 µL, 0.5 mmol) in toluene (2 mL) in O_2 atmosphere. The reaction mixture was stirred at room temperature for 15 h, maintaining an approximate distance of ~6-8 cm from two 14 W white LED bulbs. After completion of the reaction (monitored by TLC analysis), the reaction mixture was admixed with ethyl acetate (25 mL) and the organic layer was washed with water (20 mL). The organic layer was dried over anhydrous sodium sulfate (Na_2SO_4), and the solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel using 2% ethyl acetate in hexane to give pure 4,6-diphenyl-2-(phenylthio)nicotinonitrile (**1a**) (79 mg, 87%) (Scheme S9). The identity and purity of the product were confirmed by spectroscopic analysis.

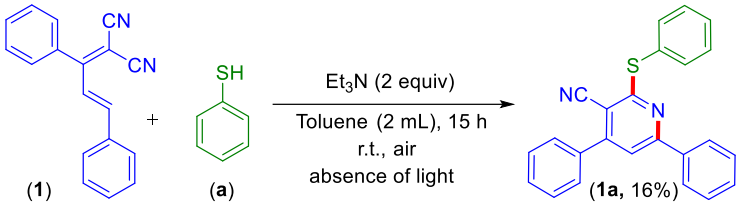


Scheme S9. Reaction in presence of O_2 atmosphere.

(E) Reaction in the Absence of white LEDs:

To an oven-dried 10 mL vial was added (*E*)-2-(1,3-diphenylallylidene)malononitrile (**1**) (0.0640 g, 0.25 mmol), thiophenol (**a**) (0.0825 g/76 µL, 0.75 mmol), and Et_3N (0.0505 g/70 µL, 0.5 mmol) in toluene (2 mL) in air atmosphere. The reaction mixture was stirred in absence of light at room temperature for 15 h. After completion of the reaction (monitored by TLC analysis), the reaction mixture was admixed with ethyl acetate (25 mL) and the organic layer was washed

with water (20 mL). The organic layer was dried over anhydrous sodium sulfate (Na_2SO_4), and the solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel using 2% ethyl acetate in hexane to give pure 4,6-diphenyl-2-(phenylthio)nicotinonitrile (**1a**) in 16% yield (15 mg) (Scheme S10). The identity and purity of the product were confirmed by spectroscopic analysis.



Scheme S10. Reaction in absence of LEDs

(F) H_2O_2 Detection in the reaction mixture[2]

H_2O_2 detection by Mohr's Salt:

In an oven-dried 10 mL borosilicate vial was added (*E*)-2-(1,3-diphenylallylidene)malononitrile (**1**) (0.0640 g, 0.25 mmol), thiophenol (**a**) (0.0825 g/76 µL, 0.75 mmol), and Et_3N (0.0505 g/70 µL, 0.5 mmol) in toluene (2 mL) in air atmosphere. The reaction mixture was stirred at room temperature, maintaining an approximate distance of ~6-8 cm from two 14 W white LED bulbs. After around 1 hour, a 100 µL solution of Mohr's Salt (10 mg in 100 µL H_2O + 1 mL CH_3CN) was added to the reaction mixture. After some time a rapid setting of $Fe(OH)_3$ floc was observed [Figure S4 (b)]. The floc observed was because of the rapid oxidation of Fe(II) to Fe(III) due to the presence of hydrogen peroxide, H_2O_2 in the medium.

(a) **(b)**

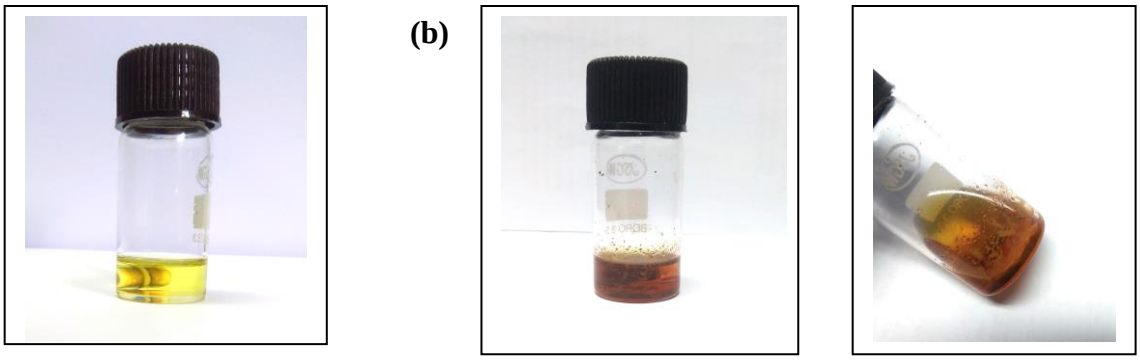


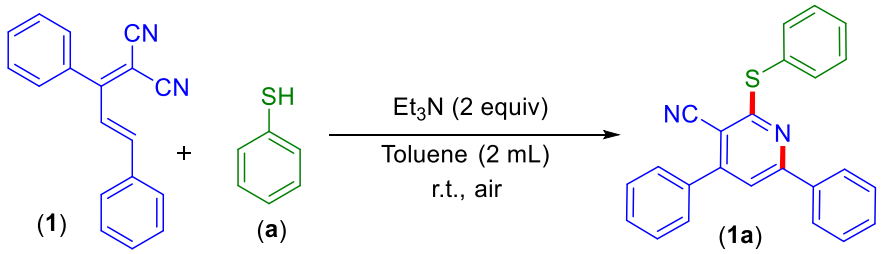
Figure S4. (a) Reaction mixture before addition of Fe(II) solution (Mohr's Salt) (b) Reaction mixture after addition of Fe(II) solution (Mohr's Salt)

7. On-off Experiments:

To an oven-dried 10 mL vial was added (*E*)-2-(1,3-diphenylallylidene)malononitrile (**1**) (0.0640 g, 0.25 mmol), thiophenol (**a**) (0.0825 g, 0.75 mmol), and Et_3N (0.0505 g, 0.5 mmol) in toluene (2 mL) in air atmosphere. The reaction mixture was stirred and irradiated by 2 x 14 W white LEDs at room temperature for 1.5 h. Then each 200 μL of the reaction aliquots was taken in a 5 mL pear-shaped round bottom flask and evaporated and co-evaporated with ethyl acetate (2 x 500μL) in a rotatory evaporator and dried under reduced pressure. The crude mixture was dissolved in 500 μL of $CDCl_3$ (containing 7% CH_3NO_2 as an internal standard.). The ^1H NMR yield of the corresponding product (**1a**) was found to be 14% (Figure S5).

Then the reaction mixture was continuously stirred in the absence of light (under dark) for 1.5 h and the same steps were repeated, the ^1H NMR yield of **1a** was 15% (Figure S6).

Again the reaction mixture was continuously stirred in the presence of 2 x 14 W light for 2 h and the same steps were repeated, the ^1H NMR yield of **1a** was found to be 33% (Figure S7) and after 2 h in the absence of light, the yield was 34% (Figure S8). Finally, when the reaction mixture was again stirred in the presence of 2 x 14 W white LEDs for 6 h, the desired product (**1a**) obtained in 52% yield as determined from ^1H NMR (Figure S9). These results suggested that continuous irradiation of visible light is essential for this transformation.



Scheme S11. On-off experiment

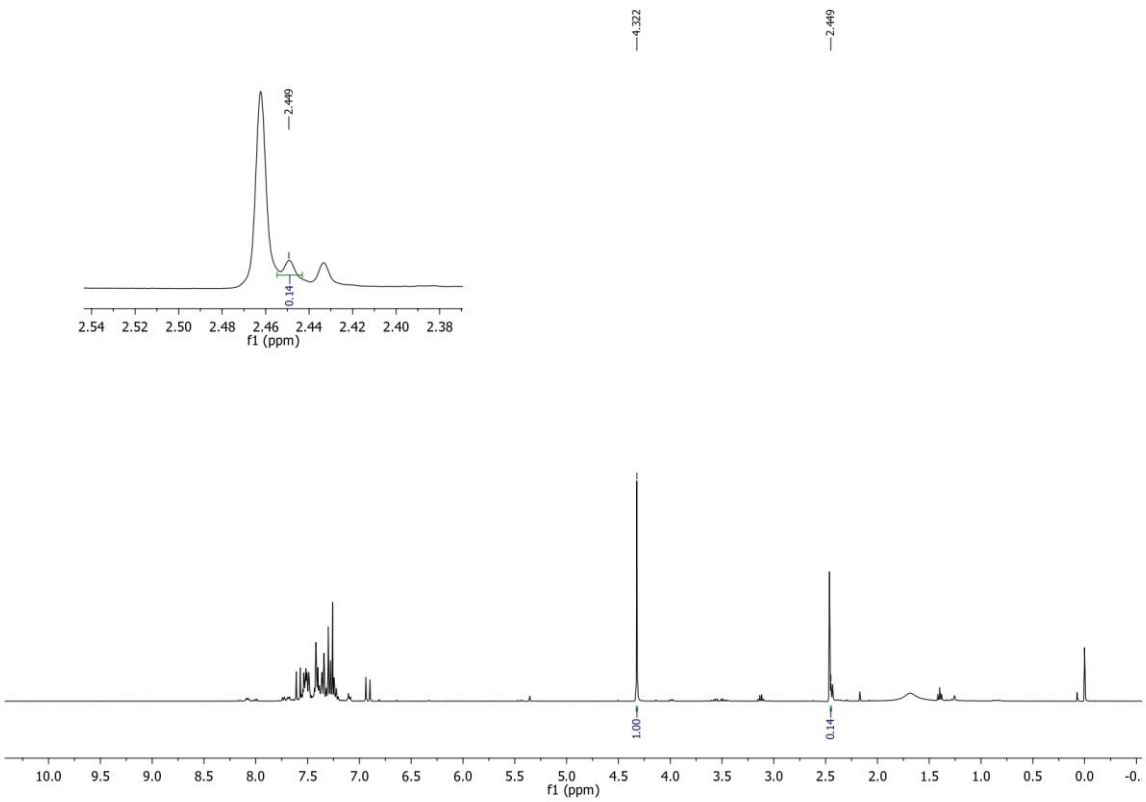


Figure S5. ^{1}H NMR of the reaction mixture after 1.5 h light on

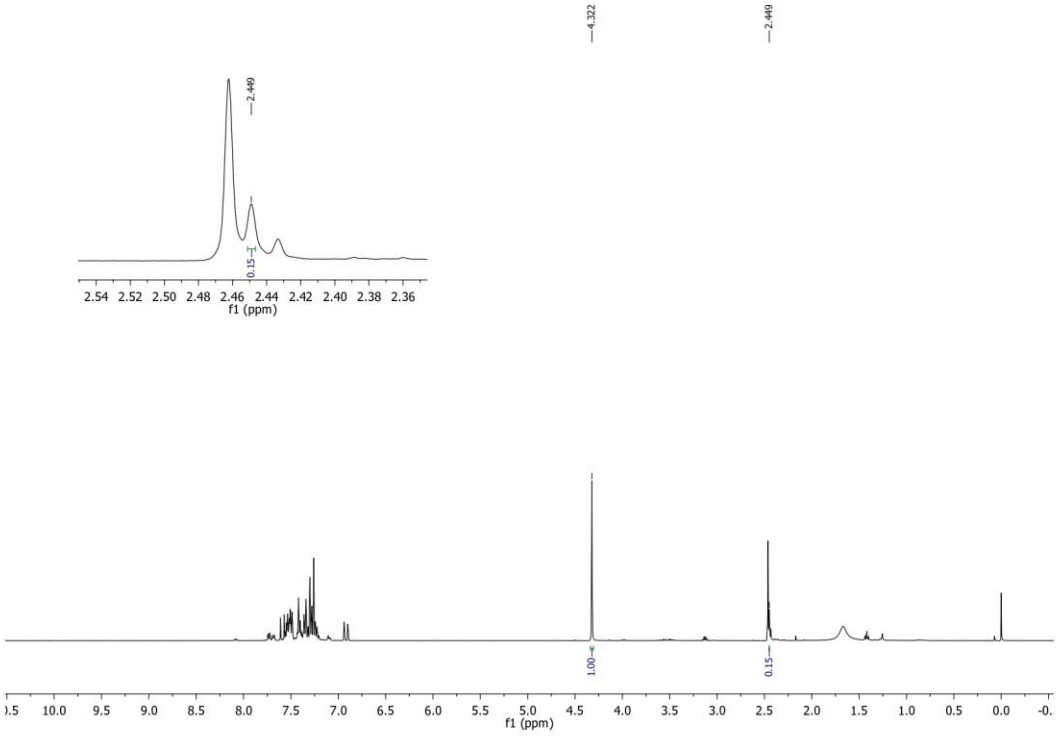


Figure S6. ^{1}H NMR of the reaction mixture after 1.5 h light off

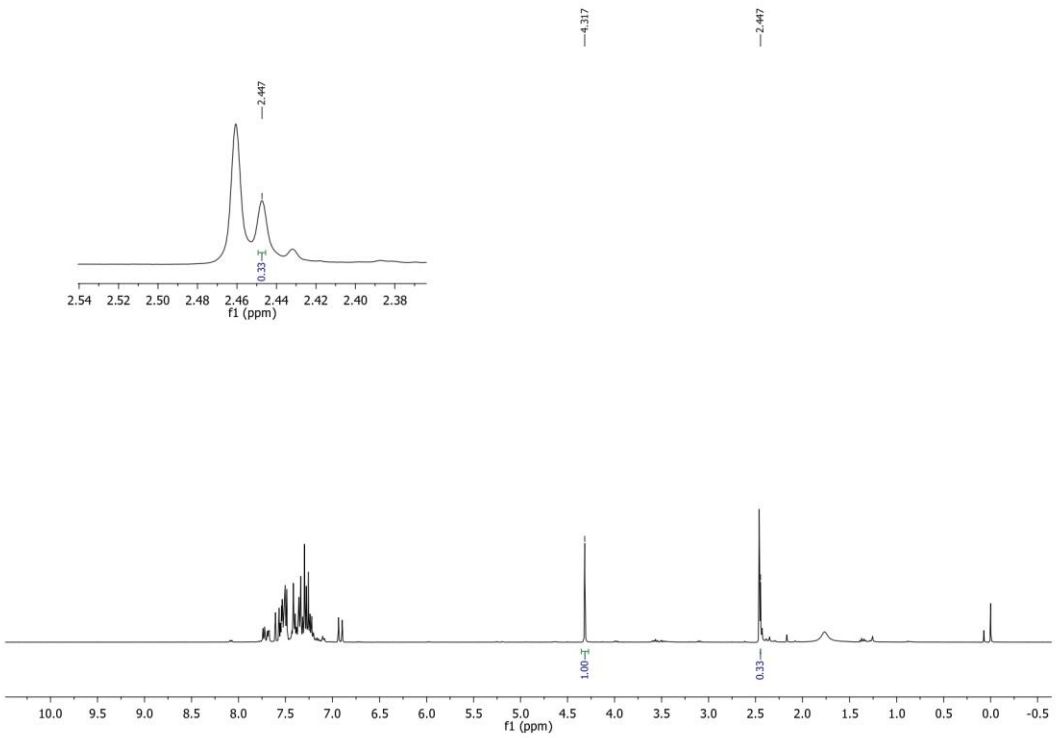


Figure S7. ^{1}H NMR of the reaction mixture after 2.0 h light on

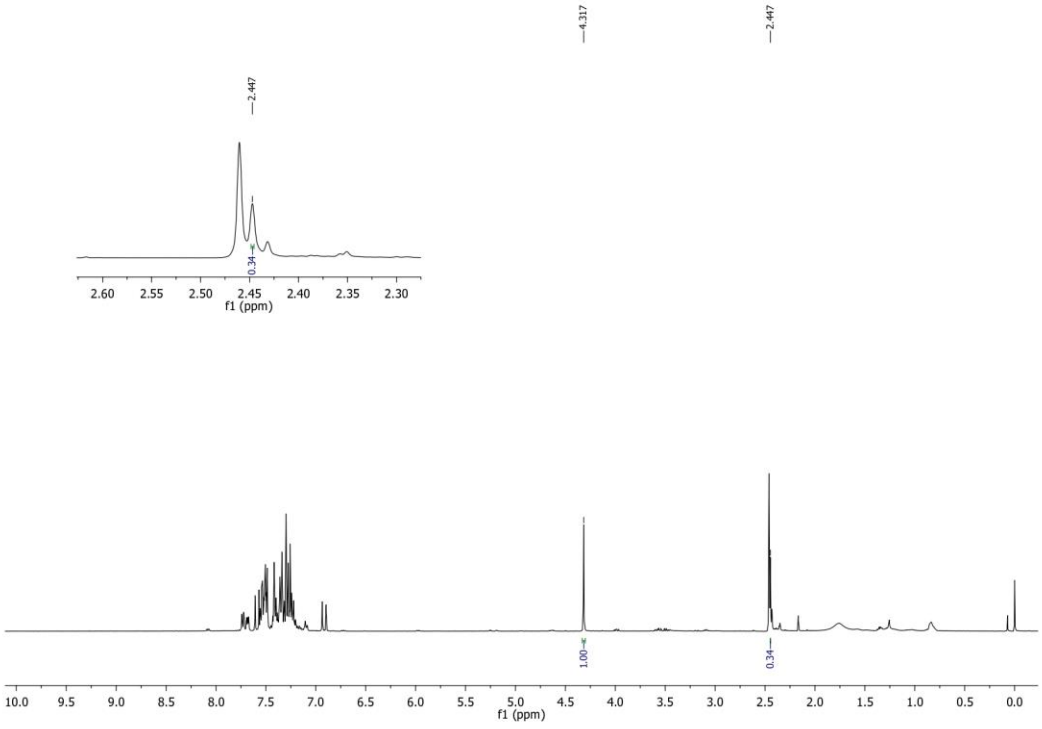


Figure S8. ^{1}H NMR of the reaction mixture after 2.0 h light off

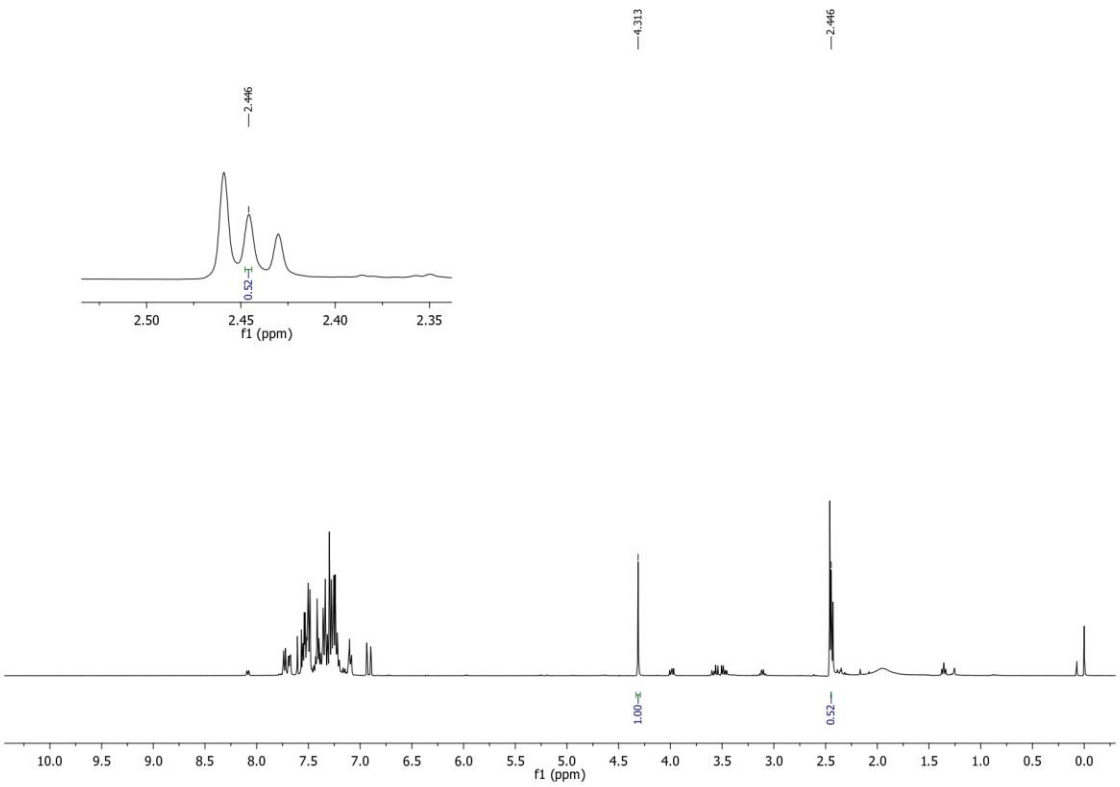


Figure S9. ^{1}H NMR of the reaction mixture after 6.0 h light on

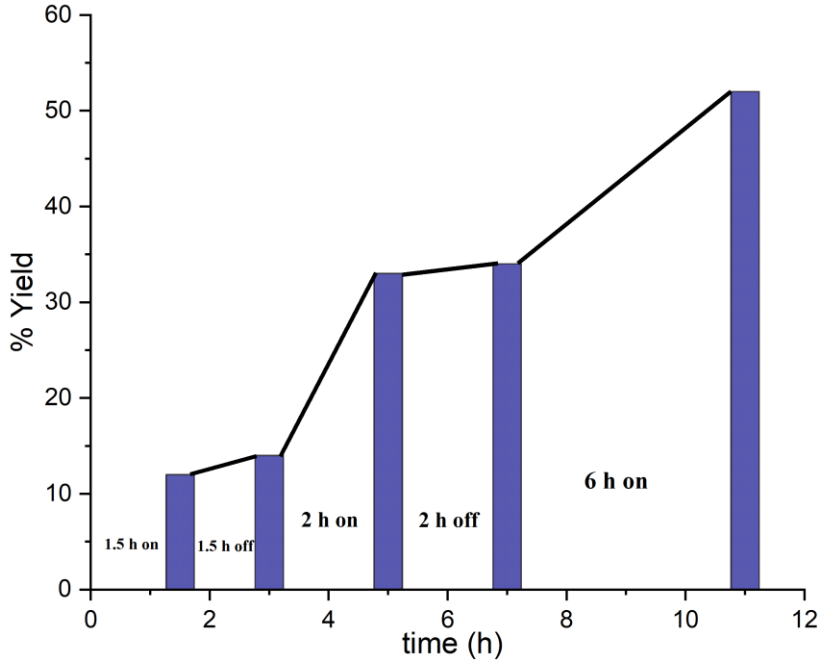


Figure S10. Plot %yield vs time (h) for On-off experiments.

8. UV-vis Experiments:[3]

A 10 mL stock solution of (*E*)-2-(1,3-diphenylallylidene)malononitrile (**1**, 5 mM), thiophenol (**a**, 5 mM) and Et_3N (5 mM) were prepared separately in toluene. At first, the UV absorption of **1**, **a** and Et_3N were taken individually none of which showed any absorption in the visible region (Figure S10). Next, 1 mL each of **1**, **a**, and Et_3N were taken in a 3 mL UV cuvette and was then exposed to the light source (white LEDs) for 10 minutes, during this period the solution turned to light yellow with an absorption maximum shift towards the visible region (λ_{max} = 414 nm), suggesting the formation of an electron donor-acceptor complex (Figure S11).

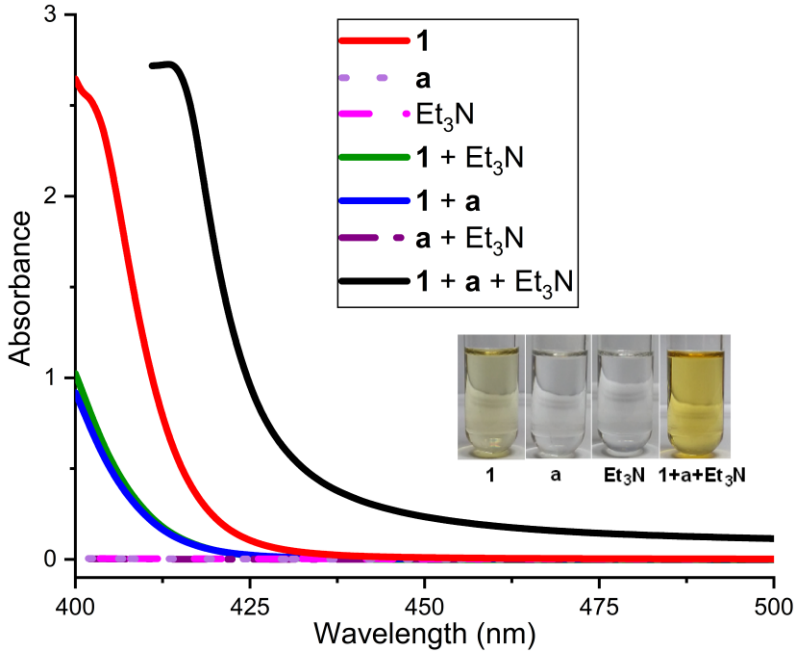


Figure S11. UV-vis spectra of EDA complex in toluene

(a) Fluorescence Studies:[4a]

In order to find further evidence for the formation of EDA pair between (*E*)-2-(1,3-diphenylallylidene)malononitrile (**1**) and PhSH (**a**), a fluorescence quenching experiment was performed. **Flask–I**. (*E*)-2-(1,3-diphenylallylidene)malononitrile (**1**) (2.56 mg) and Et_3N (1.5 μL) were taken in a 10 mL volumetric flask and the volume was adjusted to 10 mL using toluene so that the final strength of **1** and Et_3N was maintained 1 mM. **Flask–II**. In another 10 mL volumetric flask) (**1**) (2.56 mg), PhSH (**a**) (1.10 mg) and Et_3N (1.5 μL) were taken in a 10 mL volumetric flask and the volume was adjusted to 10 mL using toluene so that the final strength of

(*E*)-2-(1,3-diphenylallylidene)malononitrile (**1**), PhSH (**a**) and Et_3N was maintained 1 mM. Then 200 μL of each of the solutions (from **Flask-I** and **II**) was taken in another two 10 mL volumetric flasks (**Flask-III** and **IV**) and the volume was adjusted to 10 mL using toluene so that the final strength of both flasks was maintained 20 μM. Now **Flask-III** containing 20 μM of (*E*)-2-(1,3-diphenylallylidene)malononitrile (**1**) and Et_3N, and **Flask-IV** containing 20 μM of (*E*)-2-(1,3-diphenylallylidene)malononitrile (**1**) PhSH (**a**) and Et_3N.

For the fluorescence measurement, 2.0 mL solution from **Flask-III** was taken in a cuvette was excited at 400 nm, and the emission was observed at 432 nm. A 10 μL aliquot from **Flask-IV** [containing thiophenol (**a**)] was added sequentially and fluorescence emission was recorded each time after irradiation at regular intervals. As evident from Figure S12, a decrease in emission intensity was observed after each addition of thiophenol (**a**) {concentration 0-220 μM}. This suggests a possible interaction between **1** and thiophenol (**a**).[4]

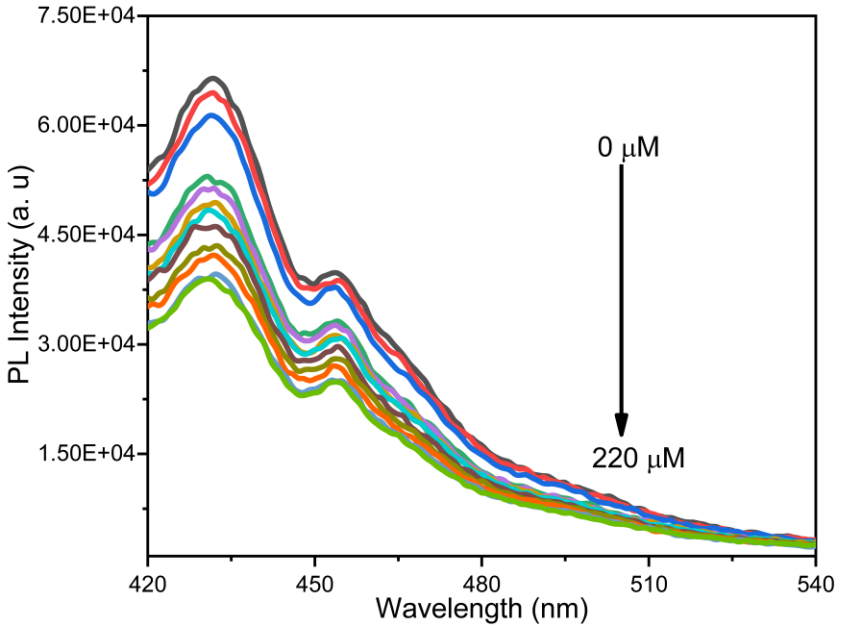


Figure S12. Fluorescence emission spectra of (1) at varied conc. of quencher thiophenol (a)

With these data, the Stern−Volmer graph was plotted using the equation $I_0/I = 1 + K_{SV}[Q]$, where I_0 and I are the integrated emission intensity in the absence and presence of a quencher and K_{sv} is the quenching constant. A linear quenching was observed (Figure S13).

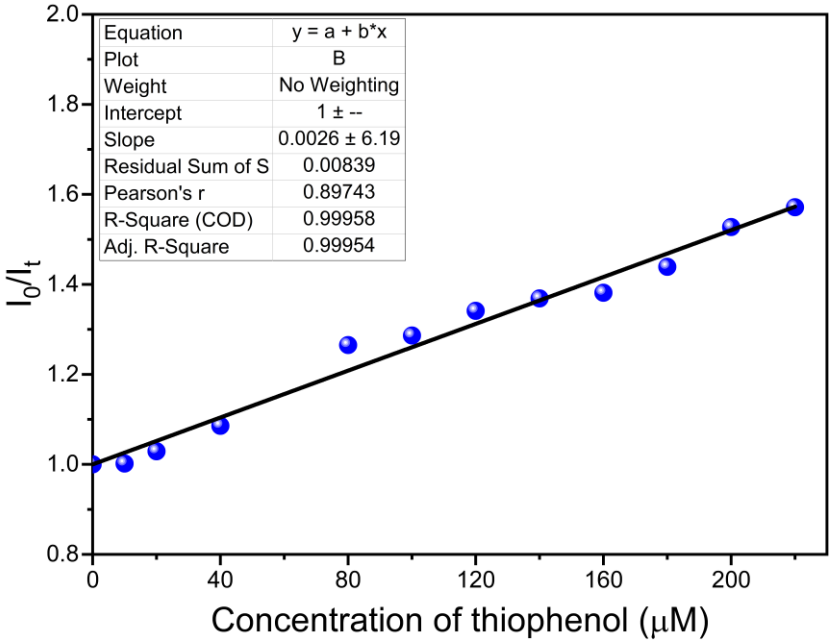


Figure S13. Stern-Volmer Plot

9. ^{19}F NMR experiments:[5]

Further to confirm the formation of the EDA complex a ^{19}F NMR experiments were performed by the preparation of DMSO-d_6 solutions containing (*E*)-2-(1-(4-fluorophenyl)-3-phenylallylidene)malononitrile (**4**), thiophenol (**a**) and Et_3N in different ratios, keeping constant the amount of (*E*)-2-(1-(4-fluorophenyl)-3-phenylallylidene)malononitrile (**4**) (0.1 mmol) and increasing the amount of **a** and Et_3N (**4** : **a** : Et_3N = 1 : 0 : 0; 1 : 1 : 1; 1 : 2 : 2; 1 : 3 : 3; 1 : 4 : 4; 1: 5 : 5, and 1 : 6 : 6). The Figure S14 shows the ^{19}F recorded spectra. The evidence of interaction between **4** and **a** is highlighted in Figures S14 and S15. Due to the interaction between F-containing substrate **4** and (**a**), the chemical shift of **4** progressively shifted downfield with increasing amounts of thiophenol (**a**) and Et_3N.

Table S2: ^{19}F NMR δ (ppm) value for the ratio of 4, a, Et_3N

Entry	**4** (mmol)	**a** (mmol)	**Et_3N** (mmol)	**4** : **a** : Et_3N	δ_F (ppm)
1	0.1	0	0	1 : 0 : 0	–109.8376
2	0.1	0.1	0.1	1 : 1 : 1	–109.8315
3	0.1	0.2	0.2	1 : 2 : 2	–109.8220
4	0.1	0.3	0.3	1 : 3 : 3	–109.8045
5	0.1	0.4	0.4	1 : 4 : 4	–109.7924
6	0.1	0.5	0.5	1 : 5 : 5	–109.7814
7	0.1	0.6	0.6	1 : 6 : 6	–109.7599

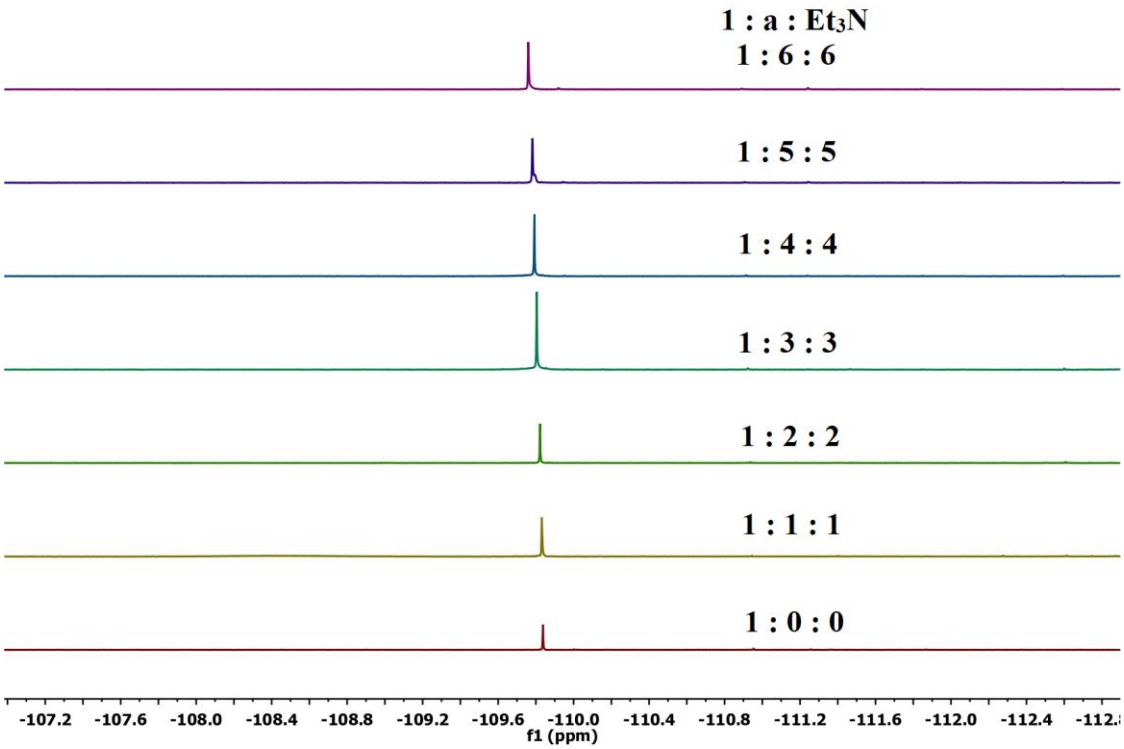


Figure S14. ^{19}F-NMR of (*E*)-2-(1-(4-fluorophenyl)-3-phenylallylidene)malononitrile (4), thiophenol (a) and Et_3N with different ratios

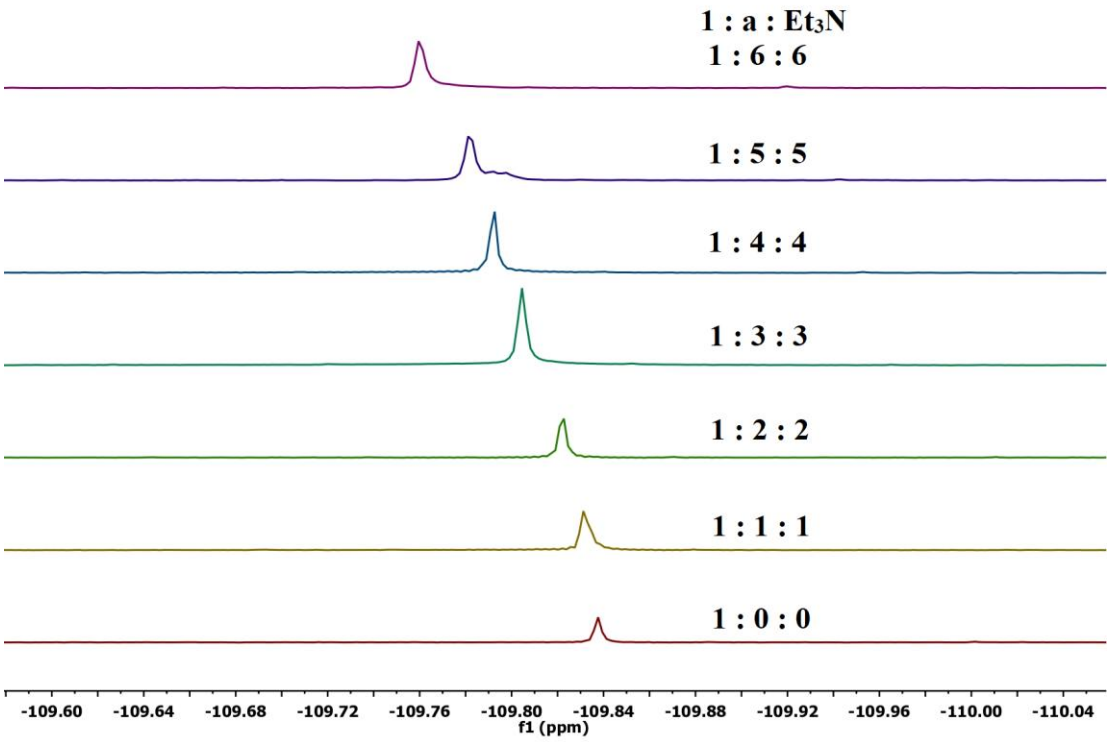


Figure S15. Evidence for the formation of EDA complex through ^{19}F NMR

10. Determination of binding constant (K_{EDA}) of EDA complex:[4]

The binding constant of the proposed EDA complex between (*E*)-2-(1,3-diphenylallylidene)malononitrile (**1**) and PhSH (**a**) in toluene containing 1 mM Et_3N, was determined spectrophotometrically using Benesi-Hildebrand methodology (Figure S16). The absorption at 405 nm corresponding to the EDA pair was measured on increasing thiophenol addition to a solution of a fixed concentration of **1** (1 mM) in 1 mM (toluene+Et_3N) solution. Keeping the constant concentration of **1** and increasing the concentration of thiophenol (100 μM, 200 μM, 300μM, …so on), the absorption spectra shifted towards the visible region. A straight line was obtained when the reciprocal of absorbance was plotted against the reciprocal of the concentration of the thiophenol (**a**). The association (binding) constant (K_{EDA}), calculated from the ratio of intercept to the slope was found to be 139.6 mM^{-1}. The calculated magnitude of the association constant for the EDA pair signifies its its binding/interaction in toluene. The Benesi–Hildebrand binding constant (K) was determined using the equation: $1/(A - A_0) = 1/(A_{max} - A) + 1/K(A_{max} - A)[M]$. Where, A_0 and A are the absorbance of (*E*)-2-(1,3-Diphenylallylidene)malononitrile in the presence of thiophenol (**a**), respectively. λ_{max} is the

absorbance at saturated concentration and [M] is the concentration of **a**. K was obtained from the ratio of the intercept to the slope in the plot of $1/(A–A_0)$ versus 1/[M] [Figure S16 (b)].

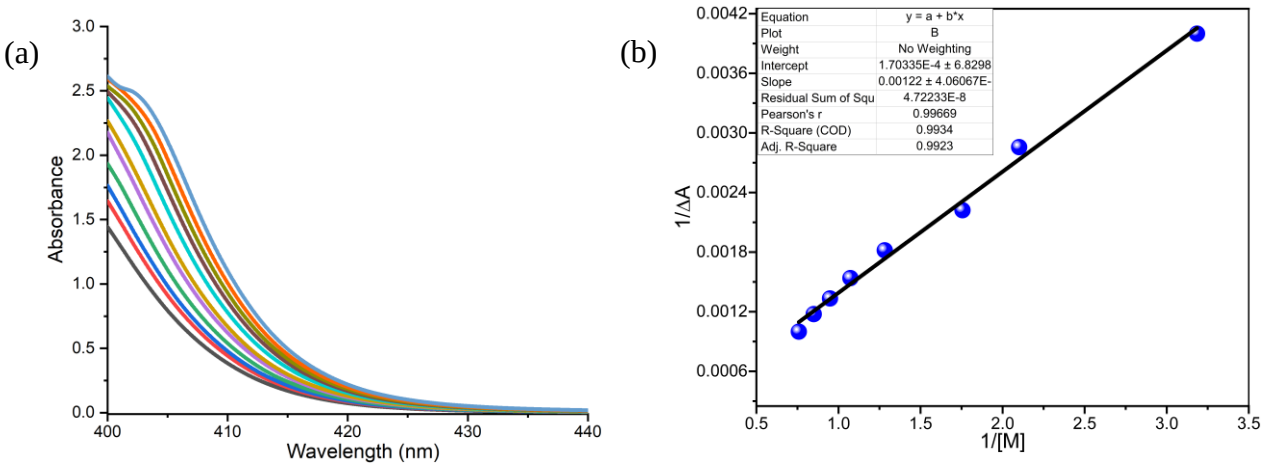


Figure S16. (a) Absorbance of mixture of (*E*)-2-(1,3-Diphenylallylidene)malononitrile (1) and thiophenol (a) with increasing amount of thiophenol in toluene+Et_3N. (b) Benesi-Hildebrand analysis of the titration curve for the complex

10. Crystallographic Information:

(A) Crystallographic Information of 2-((4-methoxyphenyl)thio)-4,6-diphenylnicotinonitrile (1d):

(i) Sample Preparation: The single crystal of compound **1d** was prepared by the slow evaporation method for which 10 mg of the compound (**1d**) was dissolved in 1 mL of DCM in a clean and dry 10 mL glass vial. MeOH (0.5 mL) was added to this solution slowly with a dropper. The mouth of the glass vial was covered with a cap having a small hole and kept for slow evaporation at room temperature. Crystals of **1d** were obtained as a transparent white needle-like crystal after around 2–3 days.

(ii) Data Collection: Diffraction data were collected at 292 K with MoKα radiation (λ = 0.71073 Å) using a Bruker Nonius SMART APEX CCD diffractometer equipped with a graphite monochromator and Apex CD camera. The SMART software was used for data collection and for indexing the reflections and determining the unit cell parameters. Data reduction and cell refinement were performed using SAINT[6,7] software and the space groups of these crystals were determined from systematic absences by XPREP and further justified by the refinement results.

The structures were solved by direct methods and refined by full-matrix least-squares calculations using SHELXTL-97[8] software. All the non-H atoms were refined in the anisotropic approximation against F^2 of all reflections.

(iii) Crystallographic description of 2-((4-methoxyphenyl)thio)-4,6-diphenylnicotinonitrile (1d):

$C_{25}H_{18}N_2OS$, crystal dimensions 0.25 x 0.21 x 0.15 mm, M_r = 394.47, orthorhombic, space group P b c a, a = 8.3336 (4), b = 18.5187 (9), c = 26.3322 (12) Å, α = 90, β = 90, γ = 90, V = 4063.8 (3) $Å^3$, Z = 8, ρ_{calcd} = 1.290 g/cm^3, μ = 0.178 mm^{-1}, F(000)= 1648.0, reflection collected / unique = 3568 / 2882, refinement method = full-matrix least-squares on F^2, final R indices [I> 2\s(I)]:R_1 = 0.0659, wR_2 = 0.1740, R indices (all data): R_1 = 0.0517, wR_2 = 0.1493, goodness of fit = 1.101. **CCDC-2252567** for **2-((4-methoxyphenyl)thio)-4,6-diphenylnicotinonitrile** (**1d**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

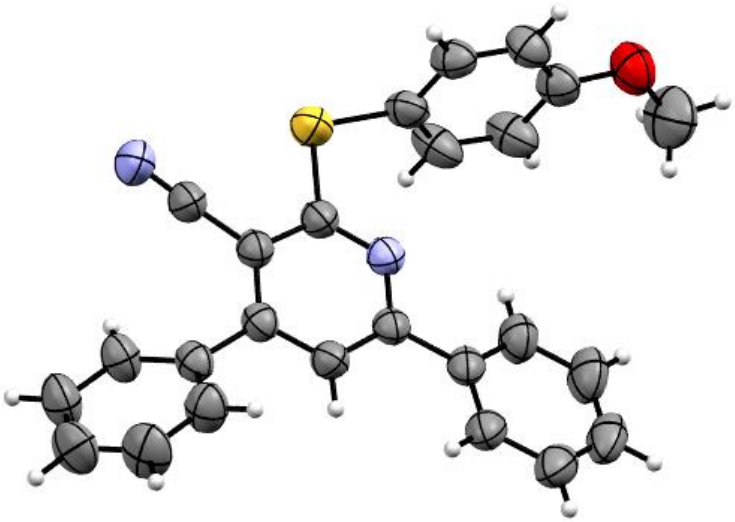


Figure S17. ORTEP diagram of 2-((4-methoxyphenyl)thio)-4,6-diphenylnicotinonitrile (1d) with 30% ellipsoid probability (CCDC 2252567)

13. References

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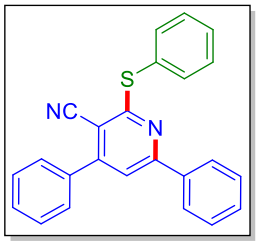
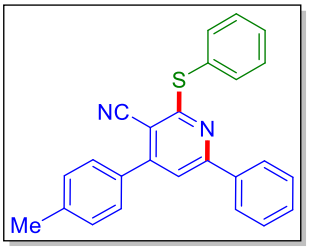
13. Spectral Data:

***4,6-Diphenyl-2-(phenylthio)nicotinonitrile (1a):*[9]**



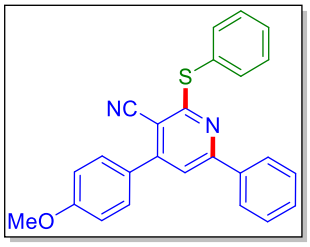
As a white solid (78 mg, 86% yield, mp 170–172 °C); Purification over a column of silica gel (2% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.74 (d, 2H, J = 7.5 Hz), 7.70–7.69 (m, 2H), 7.65–7.63 (m, 2H), 7.56–7.50 (m, 7H), 7.41–7.33 (m, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 164.2, 158.4, 154.9, 137.0, 136.4, 136.2, 130.7, 130.2, 129.6, 129.3, 129.2, 128.9, 128.6, 127.3, 116.1, 115.9, 103.3; IR (KBr, cm^{-1}): 2984, 2970, 2205, 1488, 1434, 1278, 915, 750.

***6-Phenyl-2-(phenylthio)-4-(p-tolyl)nicotinonitrile (2a):*[9]**



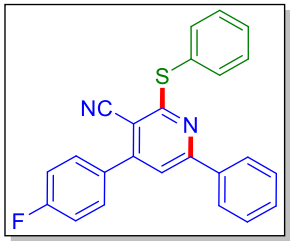
As a white solid (74 mg, 78% yield, mp 178–180 °C); Purification over a column of silica gel (2% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74–7.72 (m, 2H), 7.70–7.68 (m, 2H), 7.56–7.49 (m, 6H), 7.39–7.32 (m, 5H), 2.45 (s, 3H); ^{13}C{1H} NMR ($CDCl_3$, 100 MHz): δ 164.1, 158.3, 154.9, 140.5, 137.0, 136.2, 133.5, 130.6, 129.9, 129.6, 129.3, 129.0, 128.9, 128.4, 127.3, 116.1, 116.0, 103.2, 21.5; IR (KBr, cm^{-1}): 2959, 2917, 2217, 1730, 1523, 1262, 1023, 817.

***4-(4-Methoxyphenyl)-6-phenyl-2-(phenylthio)nicotinonitrile (3a):*[9]**



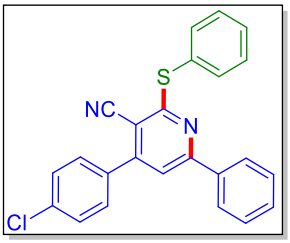
As a white solid (75 mg, 76% yield, mp 175–177 °C); Purification over a column of silica gel (4% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.73 (d, 2H, J = 7.5 Hz), 7.69–7.67 (m, 2H), 7.62 (d, 2H, J = 8.5 Hz), 7.53 (s, 1H), 7.50–7.49 (m, 3H), 7.40–7.32 (m, 3H), 7.06 (d, 2H, J = 8.5 Hz), 3.89 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 164.2, 161.3, 158.2, 154.5, 137.1, 136.2, 130.6, 130.1, 129.5, 129.3, 129.0, 128.9, 128.5, 127.3, 116.3, 115.8, 114.7, 102.9, 55.6; IR (KBr, cm^{-1}): 3034, 2823, 2237, 1455, 1265 1034, 749.

***4-(4-Fluorophenyl)-6-phenyl-2-(phenylthio)nicotinonitrile (4a):*[9]**



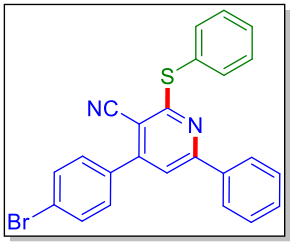
As a white solid (72 mg, 75% yield, mp 214–216 °C); Purification over a column of silica gel (2% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.76 (d, 2H, J = 7.5 Hz), 7.72–7.70 (m, 2H), 7.68–7.65 (m, 2H), 7.55–7.53 (m, 4H), 7.44–7.36 (m, 3H), 7.28 (d, 2H, J = 8.5 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 164.4, 164.0 (d, J = 249.5 Hz), 158.5, 153.8, 136.9, 136.2, 132.4 (d, J = 3.3 Hz), 130.8, 130.6 (d, J = 8.5 Hz), 129.7, 129.3, 129.0, 128.8, 127.4, 116.4 (d, J = 21.75 Hz), 115.98, 115.91, 103.2; ^{19}F NMR ($CDCl_3$, 471 MHz): δ –110.2 (s); IR (KBr, cm^{-1}): 2957, 2854, 2215, 1568, 1523, 1260, 1023, 818.

***4-(4-Chlorophenyl)-6-phenyl-2-(phenylthio)nicotinonitrile (5a):*[9]**



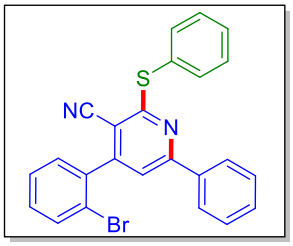
As a white solid (81 mg, 81% yield, mp 219–221 °C); Purification over a column of silica gel (2% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.72 (d, 2H, J = 7.5 Hz), 7.69–7.67 (m, 2H), 7.59–7.57 (m, 2H), 7.53–7.50 (m, 6H), 7.41–7.33 (m, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 164.5, 158.6, 153.6, 136.8, 136.7, 136.2, 134.8, 130.8, 129.9, 129.7, 129.5, 129.3, 129.0, 128.7, 127.4, 115.8, 115.7, 103.1; IR (KBr, cm^{-1}): 2962, 2884, 2212, 1595, 1565, 1259, 824.

4-(4-Bromophenyl)-6-phenyl-2-(phenylthio)nicotinonitrile (6a):



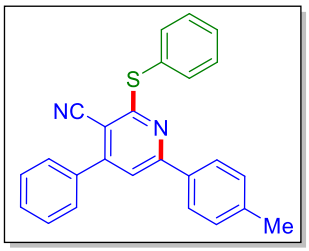
As a white solid (82 mg, 74% yield, mp 210–212 °C); Purification over a column of silica gel (2% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.72 (d, 2H, J = 8.0 Hz), 7.69–7.68 (m, 4H), 7.52–7.50 (m, 6H), 7.41–7.33 (m, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 164.5, 158.6, 153.6, 136.8, 136.2, 135.2, 132.5, 130.9, 130.1, 129.7, 129.3, 129.0, 128.7, 127.4, 124.9, 115.7, 103.0; IR (KBr, cm^{-1}): 2919, 2854, 2237, 1520, 1275, 1263, 823; HRMS (ESI/Q-TOF) (m/z) calcd for $C_{24}H_{16}BrN_2S$ $[M + H]^+$ 443.0212; found 443.0216.

4-(2-Bromophenyl)-6-phenyl-2-(phenylthio)nicotinonitrile (7a):



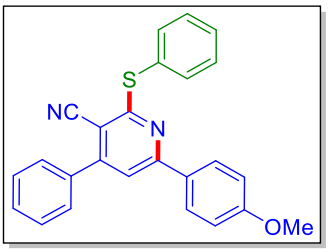
As a white solid (80 mg, 72% yield, mp 206–208 °C); Purification over a column of silica gel (2% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.76–7.71 (m, 5H), 7.53–7.52 (m, 4H), 7.47 (d, 1H, J = 7.5 Hz), 7.76–7.71 (m, 5H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 163.5, 158.2, 154.2, 137.3, 136.8, 136.1, 133.6, 131.2, 130.8, 130.5, 129.6, 129.3, 128.9, 128.6, 127.9, 127.4, 122.0, 117.0, 115.0, 104.8; IR (KBr, cm^{-1}): 2917, 2852, 2213, 1569, 1523, 1261, 1022, 742; HRMS (ESI/Q-TOF) (m/z) calcd for $C_{24}H_{16}BrN_2S$ $[M + H]^+$ 443.0212; found 443.0212.

***4-Phenyl-2-(phenylthio)-6-(p-tolyl)nicotinonitrile (8a):*[9]**



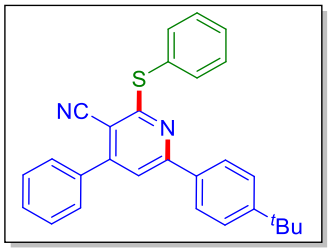
As a white solid (74 mg, 78% yield, mp 199–201 °C); Purification over a column of silica gel (2% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.70–7.68 (m, 2H), 7.63 (d, 4H, J = 8.0 Hz), 7.56–7.49 (m, 7H), 7.15 (d, 2H, J = 8.0 Hz), 2.35 (s, 3H), $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 164.1, 158.4, 154.7, 141.1, 136.5, 136.2, 134.3, 130.1, 129.7, 129.5, 129.3, 129.2, 129.0, 128.6, 127.3, 116.0, 115.7, 102.9, 21.5; IR (KBr, cm^{-1}): 2919, 2852, 2220, 1523, 1260, 1070, 820, 748.

***6-(4-Methoxyphenyl)-4-phenyl-2-(phenylthio)nicotinonitrile (9a):*[9]**



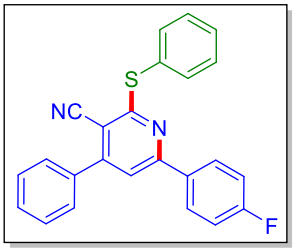
As a white solid (75 mg, 76% yield, mp 170–172 °C); Purification over a column of silica gel (4% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.69 (d, 4H, J = 8.0 Hz), 7.63–7.62 (m, 2H), 7.54–7.50 (m, 6H), 7.46 (s, 1H), 6.85 (d, 2H, J = 8.5 Hz), 3.82 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 163.9, 161.8, 158.0, 154.6, 136.5, 136.2, 130.1, 129.54, 129.50, 129.2, 129.1, 129.0, 128.9, 128.5, 116.1, 115.1, 114.3, 102.2, 55.5; IR (KBr, cm^{-1}): 2932, 2859, 2234, 1516, 1265, 749.

6-(4-(tert-Butyl)phenyl)-4-phenyl-2-(phenylthio)nicotinonitrile (10a):



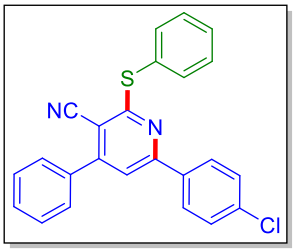
As a white solid (76 mg, 72% yield, mp 144–146 °C); Purification over a column of silica gel (4% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.71–7.70 (m, 4H), 7.66–7.64 (m, 2H), 7.56–7.52 (m, 7H), 7.39 (d, 2H, J = 8.5 Hz), 1.34 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 164.0, 158.4, 154.7, 154.2, 136.5, 136.1, 134.2, 130.1, 129.5, 129.2, 129.1, 129.0, 128.5, 127.1, 125.9, 116.0, 115.8, 102.9, 34.9, 31.3; IR (KBr, cm^{-1}): 2954, 2850, 2212, 1611, 1567, 1477, 1262, 1021, 844; HRMS (ESI/Q-TOF) (m/z) calcd for $C_{28}H_{25}N_2S$ $[M + H]^+$ 421.1733; found 421.1736.

***6-(4-Fluorophenyl)-4-phenyl-2-(phenylthio)nicotinonitrile (11a):*[9]**



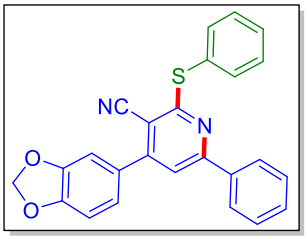
As a white solid (70 mg, 73% yield, mp 215–217 °C); Purification over a column of silica gel (2% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.72 (t, 2H, J = 6.75 Hz), 7.67 (d, 2H, J = 7.0 Hz), 7.63–7.62 (m, 2H), 7.55–7.54 (m, 3H), 7.50 (d, 4H, J = 8.0 Hz), 7.02 (t, 2H, J = 8.5 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 164.5 (d, J = 250 Hz), 164.4, 157.3, 155.0, 136.3, 136.2, 133.2 (d, J = 3.1 Hz), 130.3, 129.7, 129.5, 129.4, 129.3, 129.2, 128.9, 128.5, 116.1, 115.9, 115.8, 115.7, 103.3; ^{19}F NMR ($CDCl_3$, 471 MHz): δ –109.9 (s); IR (KBr, cm^{-1}): 2918, 2824, 2215, 1443, 1260, 1024, 748.

***6-(4-Chlorophenyl)-4-phenyl-2-(phenylthio)nicotinonitrile (12a):*[9]**



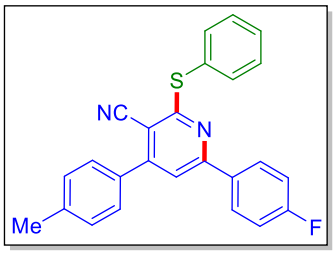
As a white solid (77 mg, 77% yield, mp 223–225 °C); Purification over a column of silica gel (2% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.68–7.62 (m, 6H), 7.55–7.49 (m, 7H), 7.31 (d, 2H, J = 8.5 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 164.5, 157.2, 155.1, 137.0, 136.4, 136.3, 135.5, 130.3, 129.7, 129.4, 129.3, 129.2, 128.8, 128.7, 128.6, 115.9, 115.8, 103.6; IR (KBr, cm^{-1}): 2929, 2849, 2217, 1566, 1520, 1260, 1091, 835.

4-(Benzo[d][1,3]dioxol-5-yl)-6-phenyl-2-(phenylthio)nicotinonitrile (13a):



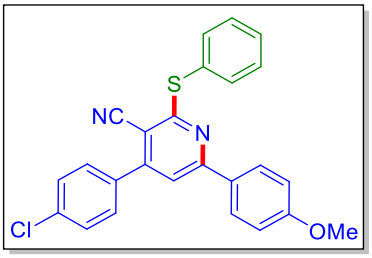
As a white solid (76 mg, 74% yield, mp 199–201 °C); Purification over a column of silica gel (2% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.72 (d, 2H, J = 7.5 Hz), 7.69–7.67 (m, 2H), 7.50–7.49 (m, 4H), 7.38–7.32 (m, 3H), 7.14 (d, 1H, J = 8.0 Hz), 7.10 (s, 1H), 6.96 (d, 1H, J = 8.0 Hz), 6.06 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 164.3, 158.3, 154.4, 149.5, 148.5, 137.0, 136.2, 130.6, 130.1, 129.6, 129.3, 129.0, 128.9, 127.3, 123.0, 116.0, 115.9, 109.0, 108.9, 103.1, 101.9; IR (KBr, cm^{-1}): 2959, 2848, 2210, 1525, 1240, 1030, 751; HRMS (ESI/Q-TOF) (m/z) calcd for $C_{25}H_{17}N_2O_2S$ $[M + H]^+$ 409.1005; found 409.1007.

6-(4-Fluorophenyl)-2-(phenylthio)-4-(p-tolyl)nicotinonitrile (14a):



As a white solid (69 mg, 70% yield, mp 201–203 °C); Purification over a column of silica gel (2% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.71 (t, 2H, J = 7.25 Hz), 7.67 (d, 2H, J = 7.5 Hz), 7.54−7.48 (m, 6H), 7.35 (d, 2H, J = 7.5 Hz), 7.01 (t, 2H, J = 8.5 Hz), 2.44 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 164.5 (d, J = 250.2 Hz), 164.3, 157.2, 155.0, 140.6, 136.2, 133.4, 133.3 (d, J = 3.0 Hz), 129.9, 129.6, 129.4, 129.3, 129.0, 128.4, 116.0, 115.9, 115.6, 103.2, 21.5; ^{19}F NMR ($CDCl_3$, 471 MHz): δ −110.0 (s); IR (KBr, cm^{-1}): 2921, 2852, 2214, 1598, 1507, 1224, 1153, 815; HRMS (ESI/Q-TOF) (m/z) calcd for $C_{25}H_{18}FN_2S$ $[M + H]^+$ 397.1169; found 397.1172.

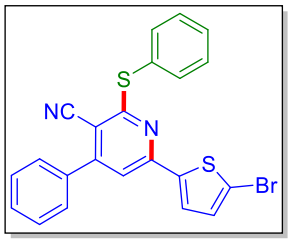
4-(4-Chlorophenyl)-6-(4-methoxyphenyl)-2-(phenylthio)nicotinonitrile (15a):



As a white solid (76 mg, 71% yield, mp 229–231 °C); Purification over a column of silica gel (4% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.69–7.66 (m, 4H), 7.57–7.49 (m, 7H), 7.42 (s, 1H), 6.84 (d, 2H, J = 8.5 Hz), 3.82 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 164.3, 162.1, 158.3, 153.4, 136.5, 136.2, 135.0, 129.9, 129.6, 129.4, 129.3, 129.1, 129.0, 115.9, 114.9, 114.4, 102.2, 55.6; IR (KBr, cm^{-1}): 3017, 2923, 2237, 1955, 1468, 1278,

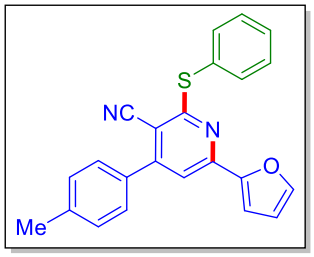
1020, 828, 753; HRMS (ESI/Q-TOF) (m/z) calcd for $C_{25}H_{18}ClN_2OS$ $[M + H]^+$ 429.0823; found 429.0824.

6-(5-Bromothiophen-2-yl)-4-phenyl-2-(phenylthio)nicotinonitrile (16a):



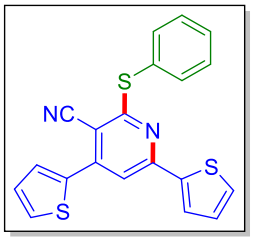
As a white solid (73 mg, 65% yield, mp 180–182 °C); Purification over a column of silica gel (2% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.65–7.63 (m, 2H), 7.61–7.59 (m, 2H), 7.54–7.51 (m, 6H), 7.27 (s, 1H), 7.22 (d, 1H, J = 4.0 Hz), 6.98 (d, 1H, J = 4.0 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 164.6, 154.7, 152.9, 144.9, 136.1, 136.0, 131.4, 130.3, 129.8, 129.4, 129.2, 128.4, 128.2, 127.0, 118.7, 115.7, 113.8, 102.7; IR (KBr, cm^{-1}): 3059, 2917, 2215, 1567, 1517, 1264, 1065, 869, 732; HRMS (ESI/Q-TOF) (m/z) calcd for $C_{22}H_{14}BrN_2S_2$ $[M + H]^+$ 448.9776; found 448.9775.

6-(Furan-2-yl)-2-(phenylthio)-4-(p-tolyl)nicotinonitrile (17a):



As a yellow solid (51 mg, 55% yield, mp 165–167 °C); Purification over a column of silica gel (2% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.67–7.65 (m, 2H), 7.54 (d, 2H, J = 7.5 Hz), 7.49–7.48 (m, 4H), 7.44 (s, 1H), 7.33 (d, 2H, J = 8.0 Hz), 6.61 (d, 1H, J = 3.5 Hz), 6.46–6.43 (m, 1H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 164.2, 154.8, 152.7, 150.2, 144.9, 140.5, 136.0, 133.3, 129.8, 129.5, 129.1, 128.9, 128.4, 116.1, 113.9, 112.7, 112.6, 102.3, 21.5; IR (KBr, cm^{-1}): 2922, 2854, 2215, 1598, 1273, 1008, 745; HRMS (ESI/Q-TOF) (m/z) calcd for $C_{23}H_{17}N_2OS$ $[M + H]^+$ 369.1056; found 369.1052.

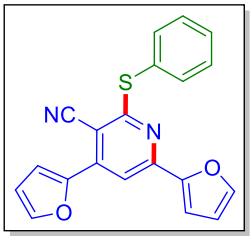
2-(Phenylthio)-4,6-di(thiophen-2-yl)nicotinonitrile (18a):



As a white solid (50 mg, 53% yield, mp 136–138 °C); Purification over a column of silica gel (2% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.89 (d, 1H, J = 3.5 Hz), 7.66–7.64 (m, 2H), 7.55 (d, 1H, J = 5.5 Hz), 7.50–7.49 (m, 4H), 7.43 (s, 1H), 7.38 (d, 1H, J = 5.0 Hz), 7.21 (t, 1H, J = 4.5 Hz), 7.04 (t, 1H, J = 4.25 Hz);

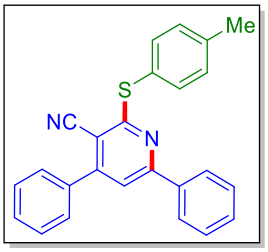
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 165.1, 153.9, 146.2, 143.2, 137.3, 136.2, 130.8, 129.7, 129.6, 129.4, 129.3, 128.9, 128.5, 128.4, 127.3, 116.4, 113.2, 100.1; IR (KBr, cm^{-1}): 2962, 2922, 2215, 1569, 1510, 1277, 741, 691; HRMS (ESI/Q-TOF) (m/z) calcd for $C_{20}H_{13}N_2S_3$ $[M + H]^+$ 377.0235; found 377.0235.

***4,6-Di(furan-2-yl)-2-(phenylthio)nicotinonitrile (19a):*[9]**



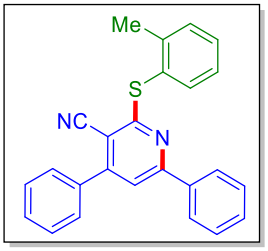
As a black solid (45 mg, 52% yield, mp 150–152 °C); Purification over a column of silica gel (2% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.80 (s, 1H), 7.64–7.62 (m, 3H), 7.61 (d, 1H, J = 3.5 Hz), 7.50 (s, 1H), 7.47–7.46 (m, 3H), 6.63 (s, 1H), 6.58 (d, 1H, J = 3.5 Hz), 6.44 (s, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 164.6, 152.7, 150.5, 148.2, 145.1, 145.0, 141.4, 136.1, 129.5, 129.1, 128.8, 116.5, 114.5, 113.0, 112.8, 112.6, 109.1, 97.1; IR (KBr, cm^{-1}): 3068, 2938, 2824, 2215, 1575, 1177, 1065.

***4,6-Diphenyl-2-(p-tolylthio)nicotinonitrile (1b):*[9]**



As a white solid (74 mg, 78% yield, mp 187–189 °C); Purification over a column of silica gel (2% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.77 (d, 2H, J = 7.0 Hz), 7.66–7.64 (m, 2H), 7.59 (d, 2H, J = 8.0 Hz), 7.56–7.54 (m, 4H), 7.42–7.35 (m, 3H), 7.32 (d, 2H, J = 8.0 Hz), 2.48 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 164.5, 158.3, 154.7, 139.8, 137.0, 136.4, 136.0, 130.6, 130.1, 130.0, 129.1, 128.8, 128.5, 127.3, 125.2, 116.0, 115.9, 103.1, 21.5; IR (KBr, cm^{-1}): 2979, 2850, 2232, 1273, 1051, 753.

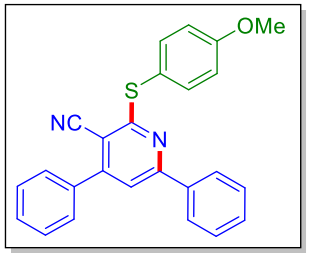
***4,6-Diphenyl-2-(o-tolylthio)nicotinonitrile (1c):*[9]**



As a white solid (70 mg, 74% yield, mp 118–120 °C); Purification over a column of silica gel (2% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.69–7.63 (m, 5H), 7.55–7.53 (m, 4H), 7.45–7.43 (m, 2H), 7.38–7.30 (m, 4H), 2.45 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 164.0, 158.2, 154.8, 143.9, 137.2, 136.9, 136.5, 130.76, 130.7, 130.3, 130.2, 129.2, 128.9, 128.6, 128.4,

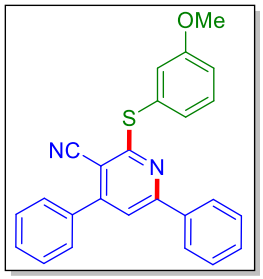
127.2, 126.8, 116.1, 115.7, 103.2, 21.1; IR (KBr, cm^{-1}): 2918, 2856, 2218, 1526, 1262, 1080, 820, 750.

2-((4-Methoxyphenyl)thio)-4,6-diphenylnicotinonitrile (1d):[9]



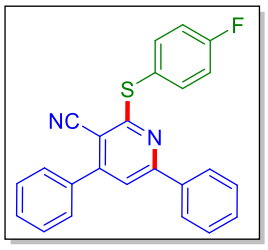
As a white solid (75 mg, 76% yield, mp 202–204 °C); Purification over a column of silica gel (2% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.77 (d, 2H, J = 7.0 Hz), 7.64–7.63 (m, 2H), 7.60 (d, 2H, J = 8.5 Hz), 7.55–7.53 (m, 4H), 7.40–7.34 (m, 3H), 7.03 (d, 2H, J = 8.5 Hz), 3.89 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 164.9, 161.0, 158.4, 154.8, 137.9, 137.1, 136.4, 130.6, 130.2, 129.2, 128.9, 128.5, 127.4, 119.4, 116.0, 114.9, 103.0, 55.6; IR (KBr, cm^{-1}): 3058, 2964, 2827, 2214, 1260, 1062.

2-((3-Methoxyphenyl)thio)-4,6-diphenylnicotinonitrile (1e):[9]



As a white solid (68 mg, 69% yield, mp 166–168 °C); Purification over a column of silica gel (3% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.81 (d, 2H, J = 7.5 Hz), 7.65–7.64 (m, 2H), 7.57–7.54 (m, 4H), 7.42–7.35 (m, 4H), 7.30–7.26 (m, 2H), 7.06 (d, 1H, J = 8.5 Hz), 3.84 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 164.0, 160.1, 158.4, 154.8, 136.9, 136.4, 130.7, 130.2, 129.9, 129.8, 129.2, 128.9, 128.5, 128.2, 127.4, 120.8, 116.2, 116.0, 115.9, 103.4, 55.6; IR (KBr, cm^{-1}): 3059, 2912, 2836, 2212, 1574, 1253, 1175, 1012, 820.

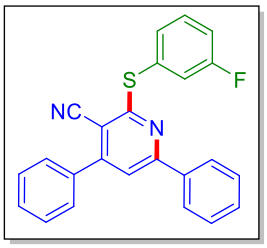
2-((4-Fluorophenyl)thio)-4,6-diphenylnicotinonitrile (1f):[9]



As a white solid (67 mg, 70% yield, mp 194–196 °C); Purification over a column of silica gel (2% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.75 (d, 2H, J = 7.5 Hz), 7.68–7.64 (m, 4H), 7.57–7.54 (m, 4H), 7.43–7.37 (m, 3H), 7.21 (t, 2H, J = 8.25 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 163.9, 163.8 (d, J = 248.7 Hz), 158.4, 154.8, 138.4 (d, J = 8.5 Hz), 136.9, 136.3, 130.8, 130.2, 129.2, 129.0, 128.5, 127.3, 124.0 (d, J = 3.5 Hz), 116.5 (d, J = 22

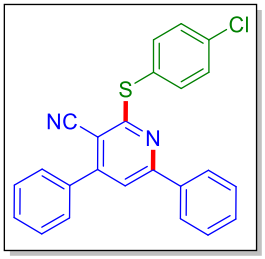
Hz), 116.2, 115.8, 103.2; ^{19}F NMR ($CDCl_3$, 471 MHz): δ –110.9 (s); IR (KBr, cm^{-1}): 2953, 2856, 2216, 1562, 1262, 1024, 750.

2-((3-Fluorophenyl)thio)-4,6-diphenylnicotinonitrile (1g):



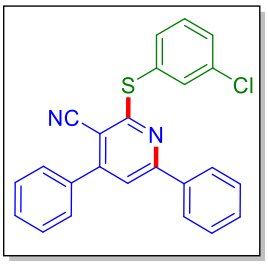
As a white solid (69 mg, 72% yield, mp 182–184 °C); Purification over a column of silica gel (2% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.78 (d, 2H, J = 7.5 Hz), 7.65–7.64 (m, 2H), 7.59 (s, 1H), 7.56–7.55 (m, 3H), 7.47–7.45 (m, 3H), 7.42–7.36 (m, 3H), 7.22 (t, 1H, J = 8.25 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 163.3, 162.9 (d, J = 247.5 Hz), 158.6, 155.0, 136.9, 136.3, 131.6 (d, J = 3.1 Hz), 130.8, 130.4 (d, J = 8.1 Hz), 130.3, 129.3, 129.0, 128.6, 127.4, 123.0, 122.8, 116.7 (d, J = 21.25 Hz), 116.5, 115.7, 103.6; ^{19}F NMR ($CDCl_3$, 471 MHz): δ –112.09 (s); IR (KBr, cm^{-1}): 2980, 2854, 2214, 1560, 1274, 1024, 752; HRMS (ESI/Q-TOF) (m/z) calcd for $C_{24}H_{16}FN_2S$ $[M + H]^+$ 383.1013; found 383.1015.

2-((4-Chlorophenyl)thio)-4,6-diphenylnicotinonitrile (1h):[9]



As a white solid (73 mg, 73% yield, mp 207–209 °C); Purification over a column of silica gel (2% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.75 (d, 2H, J = 7.0 Hz), 7.65–7.61 (m, 4H), 7.57 (s, 1H), 7.56–7.54 (m, 3H), 7.48 (d, 2H, J = 8.0 Hz), 7.42–7.37 (m, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 163.5, 158.5, 154.9, 137.3, 136.8, 136.2, 136.0, 130.8, 130.3, 129.5, 129.2, 129.0, 128.5, 127.4, 127.3, 116.4, 115.7, 103.4; IR (KBr, cm^{-1}): 2965, 2872, 2210, 1564, 1476, 1258, 1059, 760.

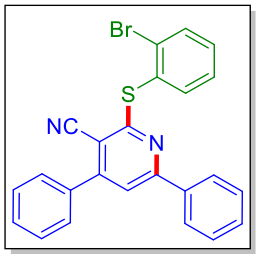
2-((3-Chlorophenyl)thio)-4,6-diphenylnicotinonitrile (1i):[9]



As a white solid (65 mg, 65% yield, mp 190–192 °C); Purification over a column of silica gel (2% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.80 (d, 2H, J = 7.0 Hz), 7.76 (s, 1H), 7.65–7.63 (m, 2H), 7.59 (s, 1H), 7.57–7.54 (m, 4H), 7.49 (d, 1H, J = 8.0 Hz), 7.43–7.37 (m, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 163.1, 158.6, 155.0, 136.9, 136.3, 135.9, 134.7, 133.9, 130.9, 130.7,

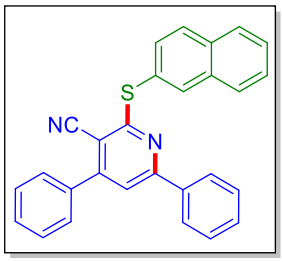
130.3, 130.2, 129.7, 129.3, 129.1, 128.6, 127.4, 116.6, 115.7, 103.6; IR (KBr, cm^{-1}): 2958, 2860, 2215, 1561, 1471, 1262, 1058, 748.

2-((2-Bromophenyl)thio)-4,6-diphenylnicotinonitrile (1j):[9]



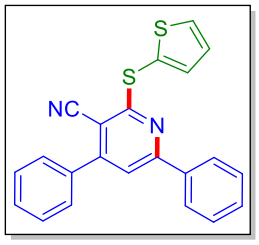
As a white solid (71 mg, 64% yield, mp 160–162 °C); Purification over a column of silica gel (2% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.82 (d, 1H, J = 7.5 Hz), 7.78 (d, 1H, J = 7.5 Hz), 7.72 (d, 2H, J = 7.5 Hz), 7.67–7.65 (m, 2H), 7.57–7.54 (m, 4H), 7.44–7.33 (m, 5H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 162.8, 158.5, 154.9, 138.2, 136.9, 136.3, 133.7, 131.5, 131.3, 130.8, 130.7, 130.2, 129.2, 128.9, 128.5, 128.2, 127.3, 116.3, 115.8, 103.4; IR (KBr, cm^{-1}): 2918, 2855, 2214, 1569, 1484, 1264, 1022, 742.

2-(Naphthalen-2-ylthio)-4,6-diphenylnicotinonitrile (1k):[9]



As a white solid (83 mg, 80% yield, mp 172–174 °C); Purification over a column of silica gel (2% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.23 (s, 1H), 7.94 (t, 2H, J = 7.5 Hz), 7.88 (d, 1H, J = 7.5 Hz), 7.72 (d, 1H, J = 8.75 Hz), 7.69 (d, 2H, J = 7.0 Hz), 7.66–7.64 (m, 2H), 7.59–7.54 (m, 6H), 7.32 (t, 1H, J = 7.5 Hz), 7.23 (t, 2H, J = 7.75 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 164.1, 158.5, 154.9, 136.9, 136.4, 135.4, 133.9, 133.6, 132.5, 130.6, 130.2, 129.2, 128.9, 128.6, 128.2, 127.9, 127.4, 127.3, 126.7, 126.3, 116.3, 116.0, 103.4; IR (KBr, cm^{-1}): 3002, 2852, 2235, 1574, 1275, 1258, 749.

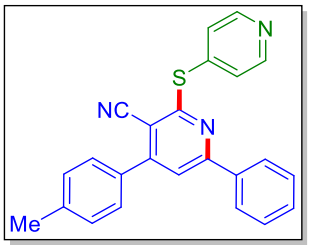
4,6-Diphenyl-2-(thiophen-2-ylthio)nicotinonitrile (1l):[9]



As a white solid (66 mg, 71% yield, mp 164–166 °C); Purification over a column of silica gel (2% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.84 (d, 2H, J = 7.0 Hz), 7.69 (d, 1H, J = 5.5 Hz), 7.64–7.63 (m, 2H), 7.58 (s, 1H), 7.56–7.54 (m, 3H), 7.42–7.38 (m, 4H), 7.21 (t, 1H, J = 4.2 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 163.9, 158.8, 154.8, 137.5, 136.8, 136.2, 132.8, 130.8,

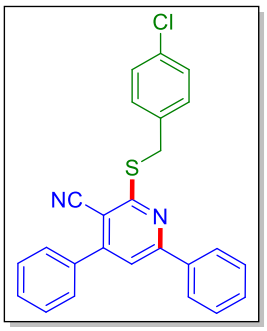
130.2, 129.2, 128.9, 128.5, 127.9, 127.4, 125.8, 116.5, 115.7, 102.9; IR (KBr, cm^{-1}): 3024, 2854, 2220, 1523, 1261, 1025, 748.

6-Phenyl-2-(pyridin-4-ylthio)-4-(p-tolyl)nicotinonitrile (2m):



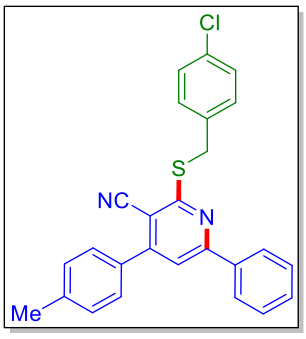
As a yellow solid (30 mg, 32% yield, mp 190–192 °C); Purification over a column of silica gel (15% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.61–7.59 (m, 3H), 7.55–7.53 (m, 4H), 7.52–7.49 (m, 3H), 7.35 (d, 3H, J = 8.0 Hz), 7.24 (s, 1H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 181.3, 162.4, 157.3, 142.0, 135.8, 134.7, 131.9, 130.7, 130.5, 130.0, 129.8, 128.3, 127.1, 119.7, 114.8, 106.0, 21.7; IR (KBr, cm^{-1}): 3064, 2924, 2220, 1635, 1486, 1190, 763; HRMS (ESI/Q-TOF) (m/z) calcd for $C_{24}H_{18}N_3S$ $[M + H]^+$ 380.1216; found 380.1214.

2-((4-Chlorobenzyl)thio)-4,6-diphenylnicotinonitrile (1n):



As a white solid (66 mg, 64% yield, mp 175–177 °C); Purification over a column of silica gel (2% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.06–8.04 (m, 2H), 7.62–7.61 (m, 2H), 7.55–7.50 (m, 7H), 7.41 (d, 2H, J = 8.0 Hz), 7.27 (d, 2H, J = 8.5 Hz), 4.63 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 163.3, 158.8, 154.8, 137.5, 136.3, 136.0, 133.4, 130.8, 130.5, 130.3, 129.3, 129.2, 128.9, 128.5, 127.6, 116.4, 115.7, 103.8, 34.3; IR (KBr, cm^{-1}): 2962, 2917, 2212, 1570, 1528, 1261, 748; HRMS (ESI/Q-TOF) (m/z) calcd for $C_{25}H_{18}ClN_2S$ $[M + H]^+$ 413.0874; found 413.0876.

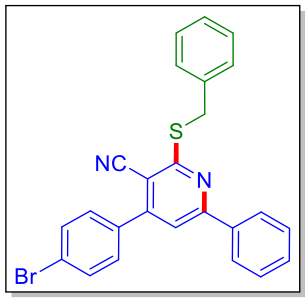
2-((4-Chlorobenzyl)thio)-6-phenyl-4-(p-tolyl)nicotinonitrile (2n):



As a white solid (66 mg, 62% yield, mp 178–180 °C); Purification over a column of silica gel (2% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.05–8.03 (m, 2H), 7.54–7.50 (m, 6H), 7.41 (d, 2H, J = 8.5 Hz), 7.33 (d, 2H, J = 8.0 Hz), 7.27 (d, 2H, J = 8.0 Hz), 4.63 (s, 2H), 2.43 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 163.2, 158.7, 154.8, 140.6, 137.6, 136.1, 133.44, 133.40, 130.7,

130.5, 129.9, 129.1, 128.9, 128.5, 127.5, 116.3, 116.0, 103.7, 34.3, 21.5; IR (KBr, cm^{-1}): 2959, 2917, 2216, 1525, 1265, 1024, 745; HRMS (ESI/Q-TOF) (m/z) calcd for $C_{26}H_{20}ClN_2S$ $[M + H]^+$ 427.1030; found 427.1030.

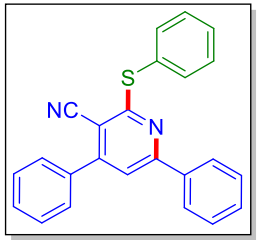
2-(Benzylthio)-4-(4-bromophenyl)-6-phenylnicotinonitrile (6o):

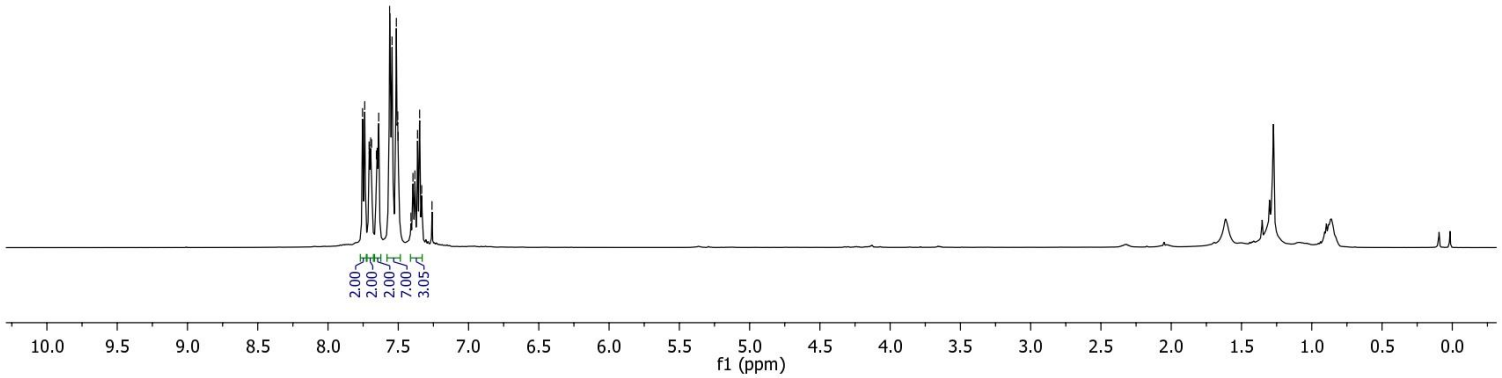


As a white solid (59 mg, 52% yield, mp 215–217 °C); Purification over a column of silica gel (2% EtOAc in hexane); ^1H NMR ($CDCl_3$, 500 MHz): δ 8.12 (s, 1H), 7.72 (d, 2H, J = 7.5 Hz), 7.57–7.52 (m, 6H), 7.38–7.31 (m, 6H), 4.73 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 164.1, 159.0, 153.5, 137.4, 137.1, 135.2, 132.5, 130.9, 130.1, 129.8, 129.5, 129.2, 128.8, 127.6, 124.9, 115.8, 115.6, 103.4, 35.1; IR (KBr, cm^{-1}): 2923, 2850, 2218, 1520, 1263, 824, 748; HRMS (ESI/Q-TOF) (m/z) calcd for $C_{25}H_{18}BrN_2S$ $[M + H]^+$ 457.0369; found 457.0370

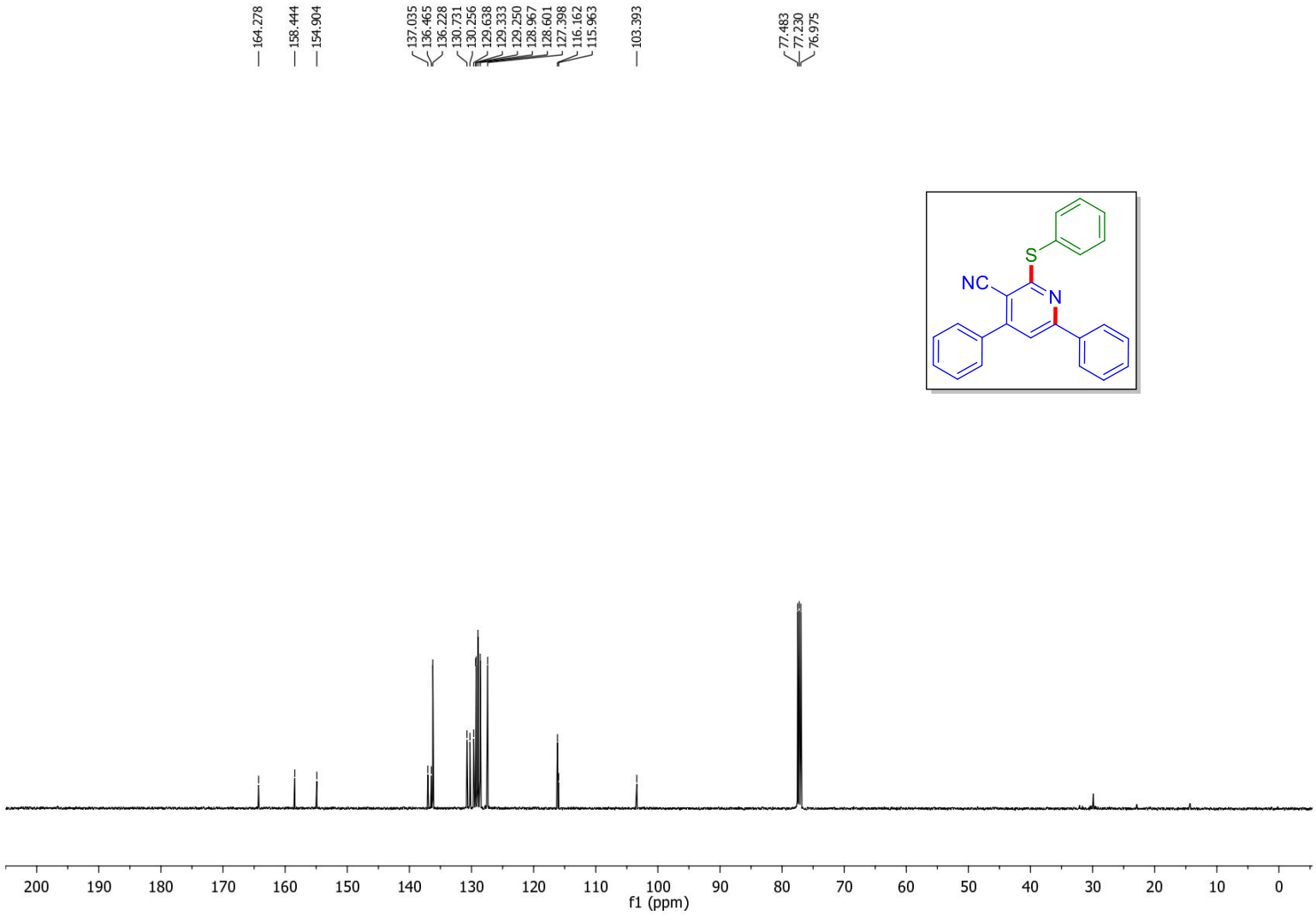
14. Spectra of all compounds:

4,6-Diphenyl-2-(phenylthio)nicotinonitrile (1a): ^{1}H NMR ($CDCl_3$, 500 MHz)

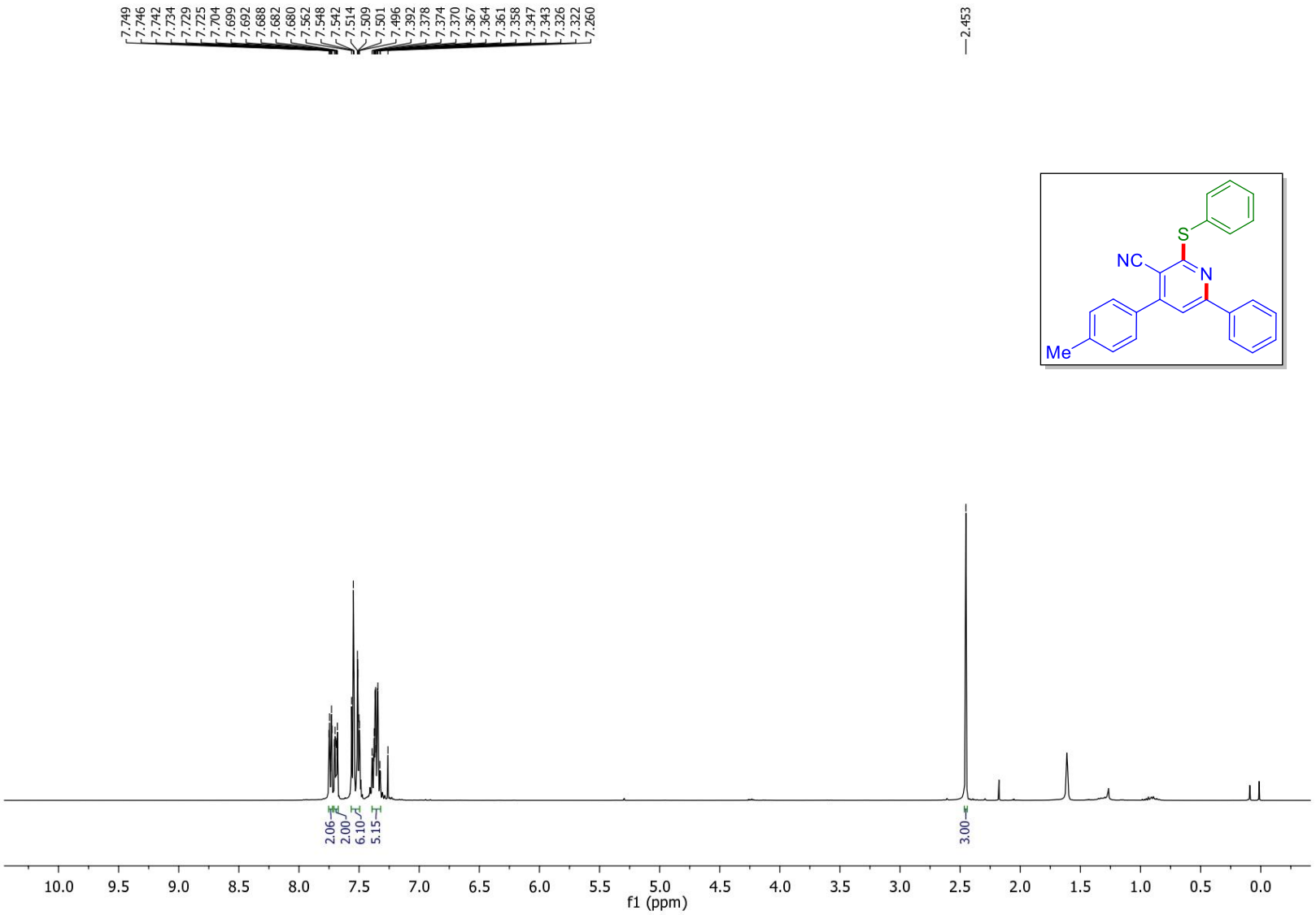




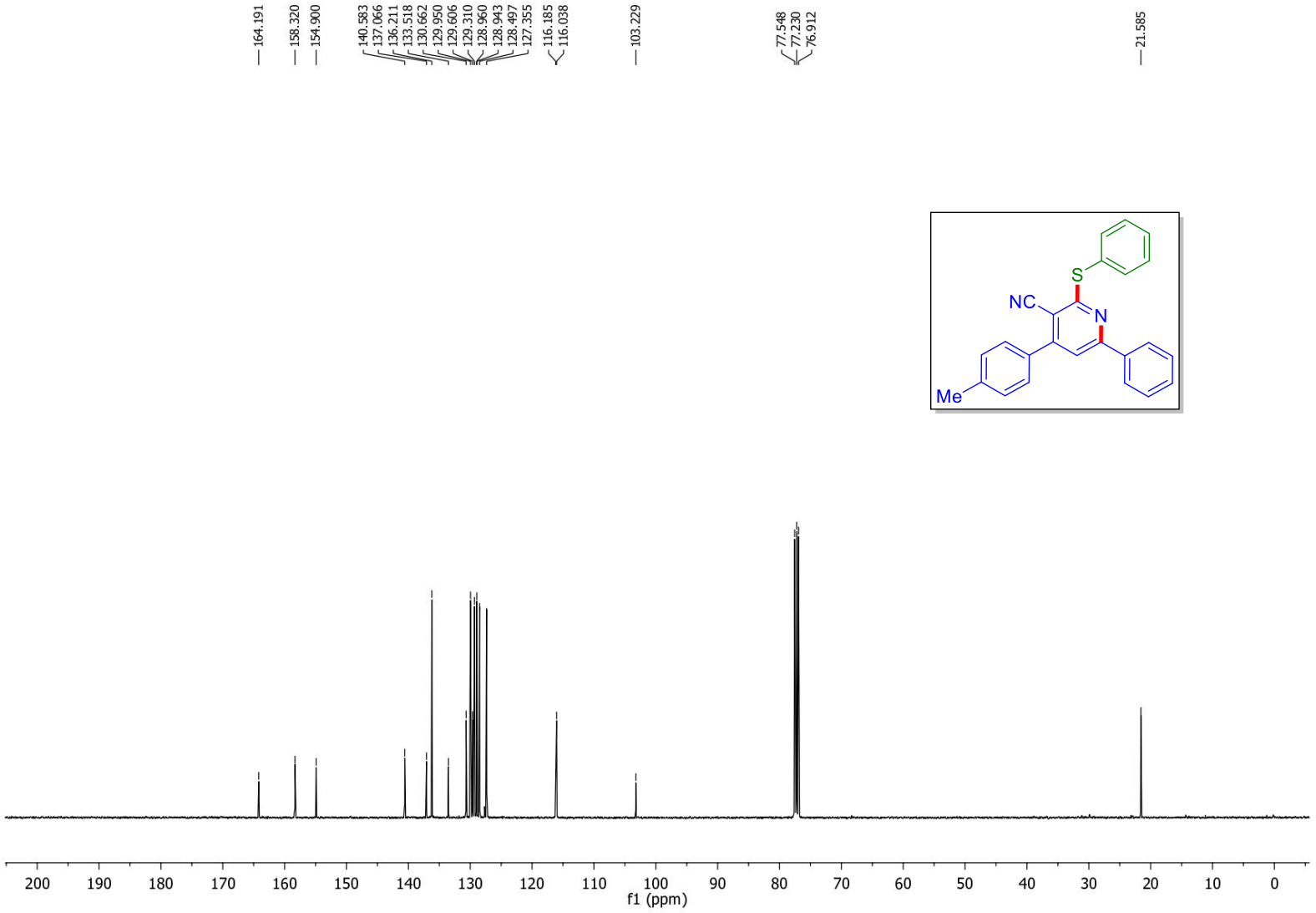
4,6-Diphenyl-2-(phenylthio)nicotinonitrile (1a):$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



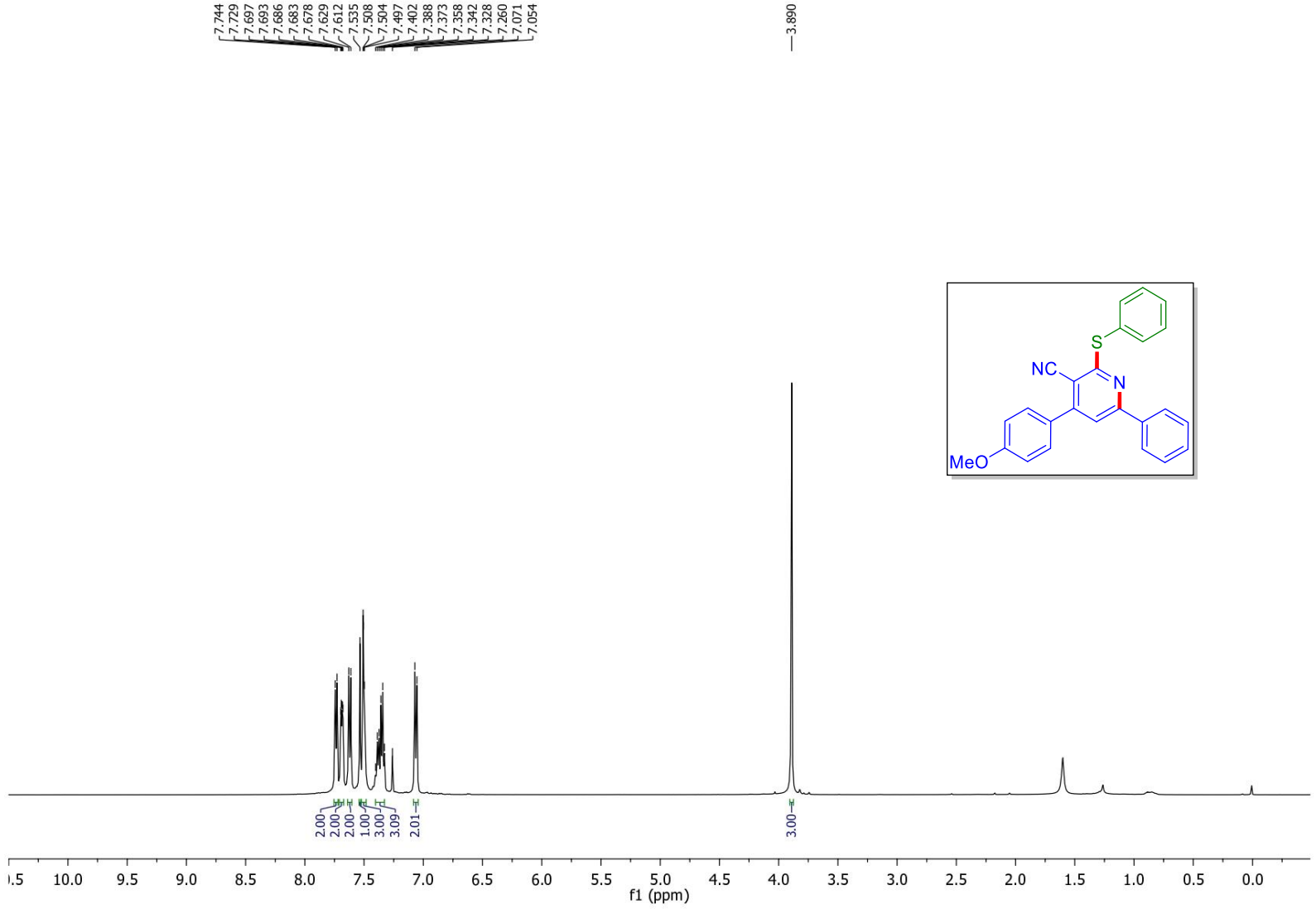
6-Phenyl-2-(phenylthio)-4-(p-tolyl)nicotinonitrile (2a): ^{1}H NMR (CDCl$_3$, 400 MHz)



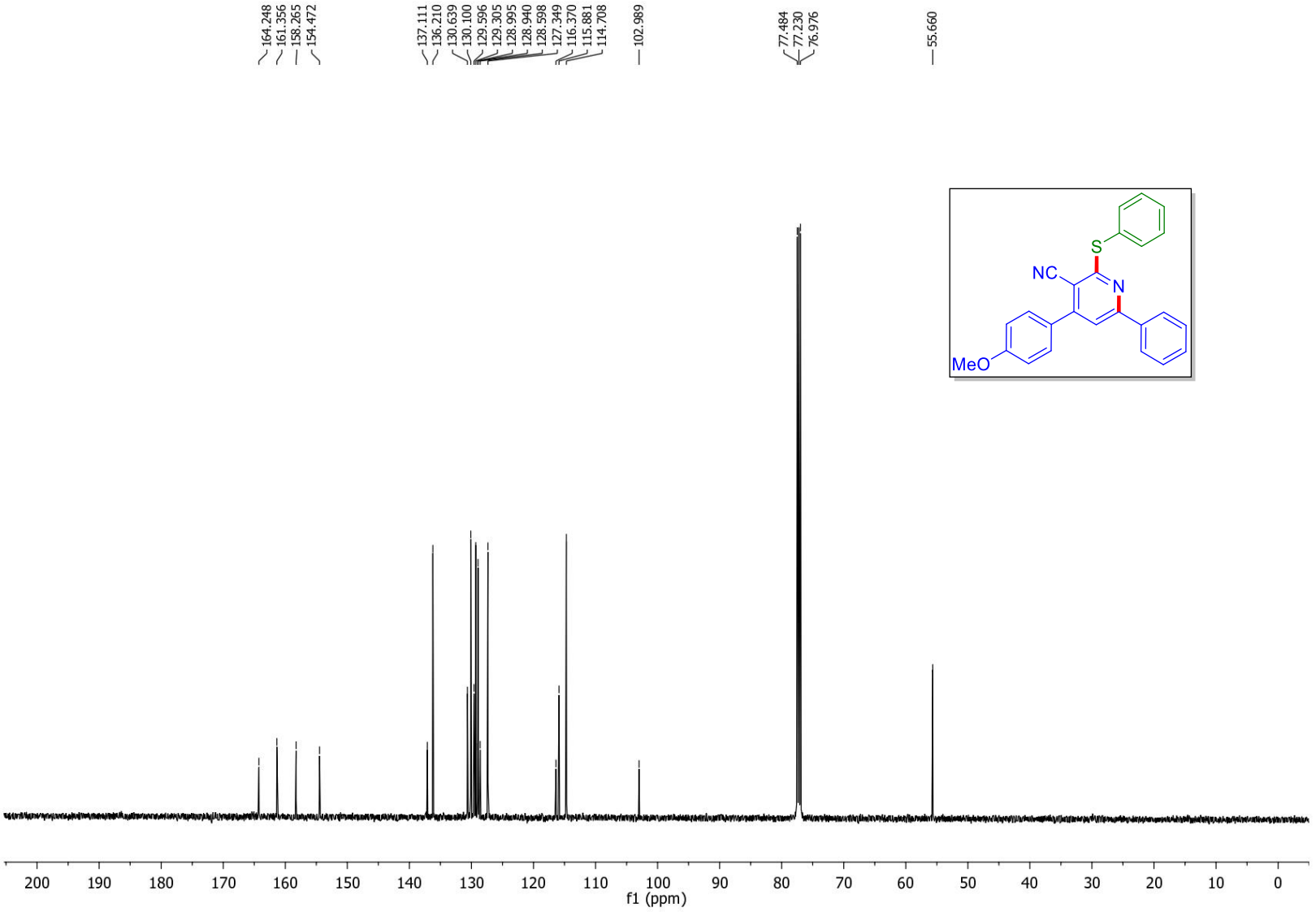
6-Phenyl-2-(phenylthio)-4-(p-tolyl)nicotinonitrile (2a) : $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)



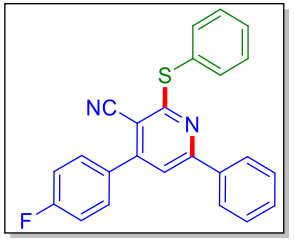
4-(4-Methoxyphenyl)-6-phenyl-2-(phenylthio)nicotinonitrile (3a): ^{1}H NMR (CDCl$_3$, 500 MHz)

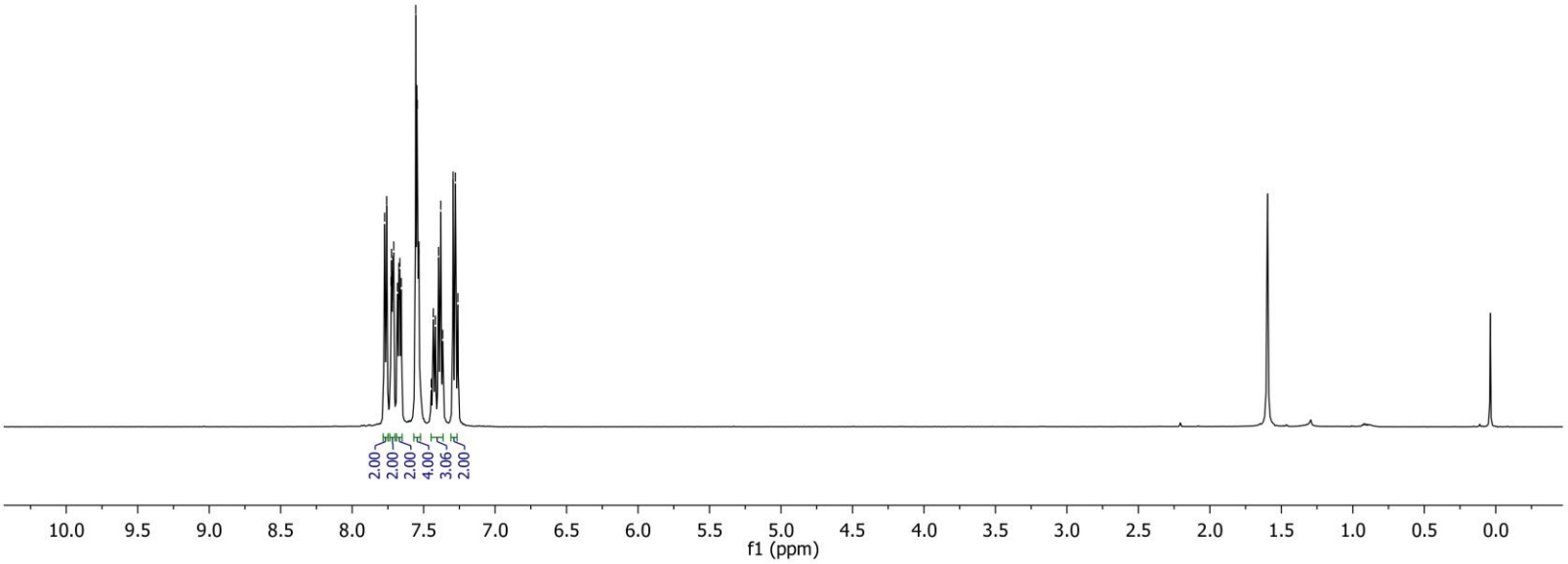


4-(4-Methoxyphenyl)-6-phenyl-2-(phenylthio)nicotinonitrile (3a): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)

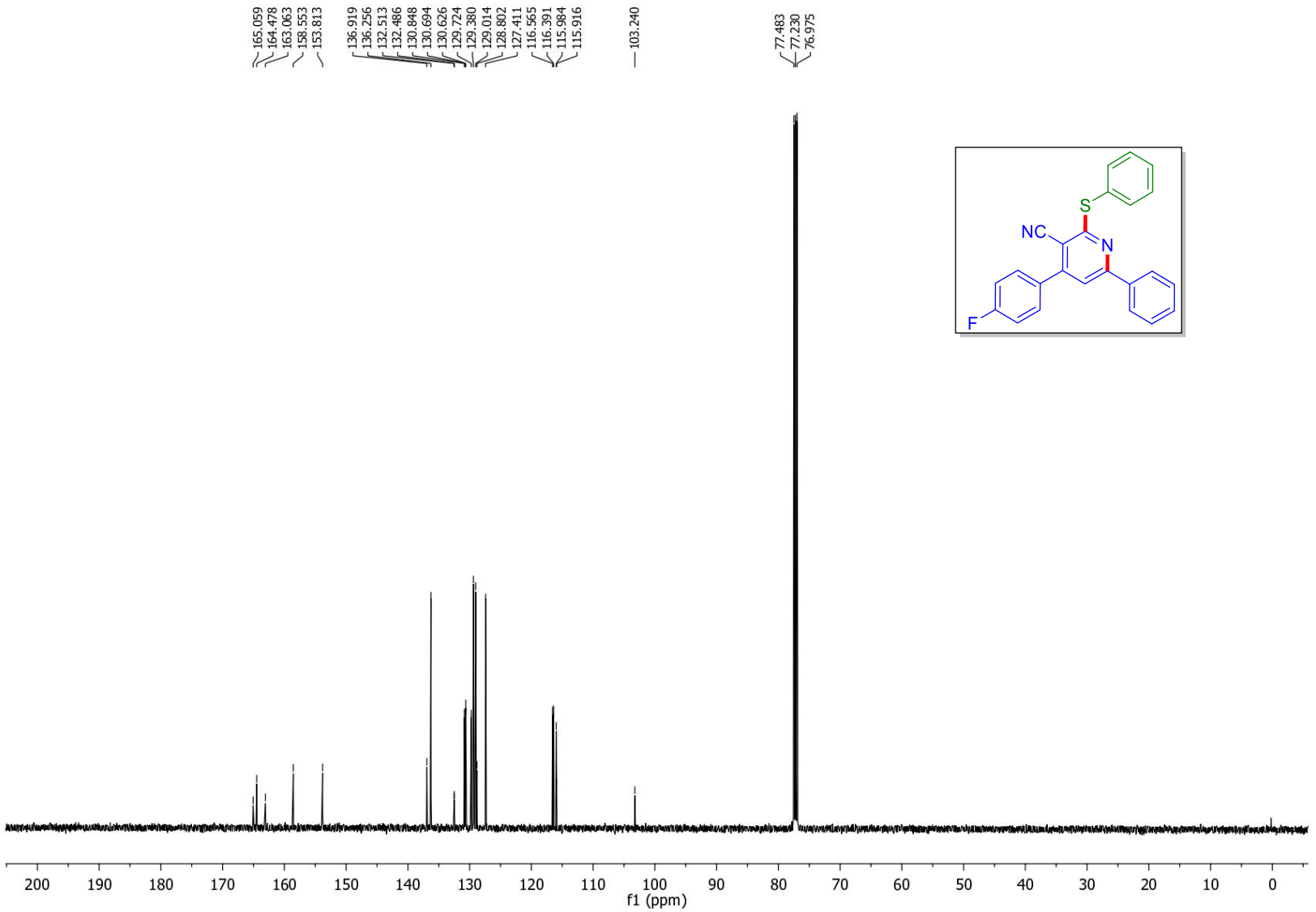


4-(4-Fluorophenyl)-6-phenyl-2-(phenylthio)nicotinonitrile (4a): ^{1}H NMR ($CDCl_3$, 500 MHz)

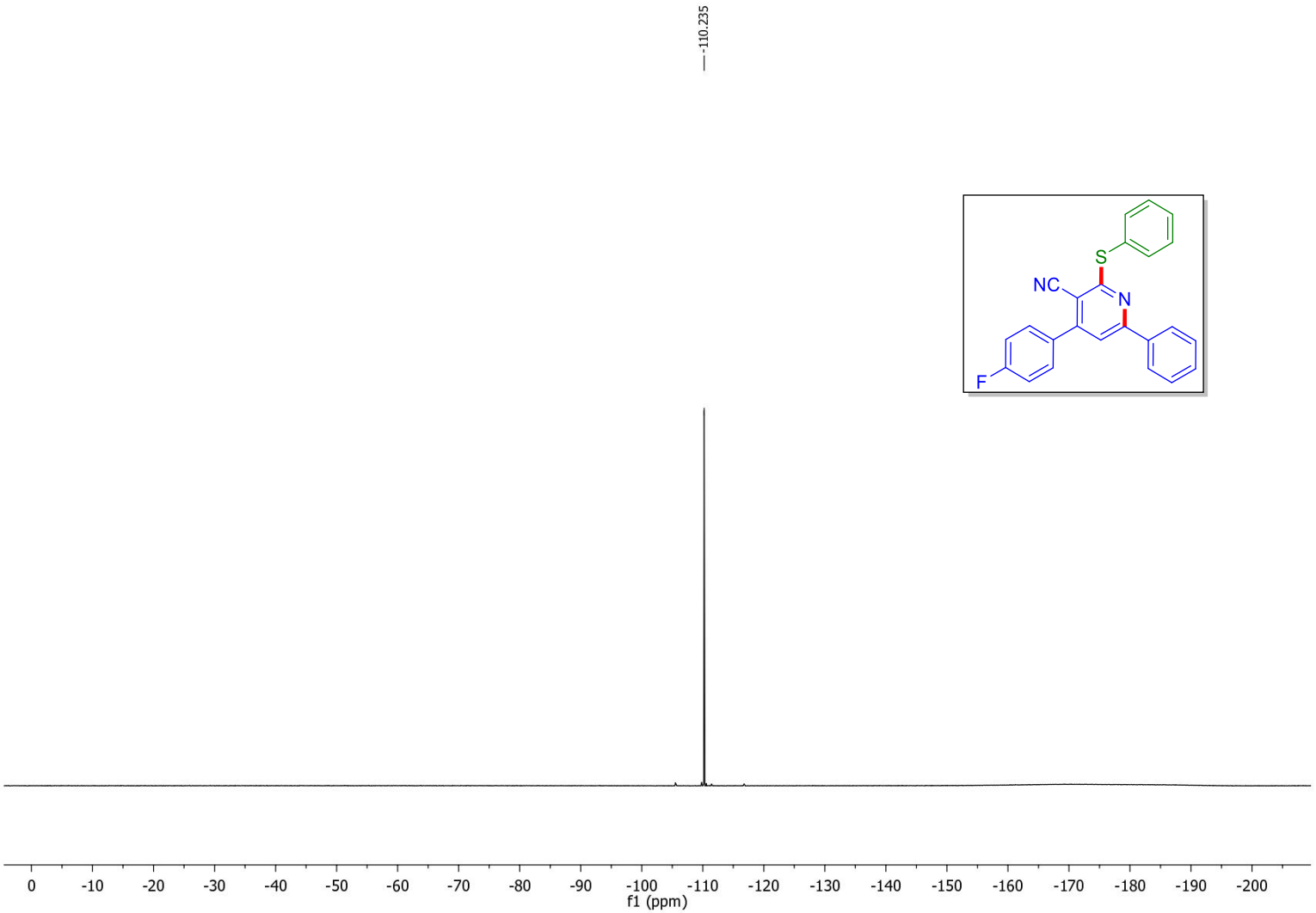




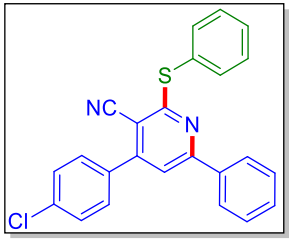
4-(4-Fluorophenyl)-6-phenyl-2-(phenylthio)nicotinonitrile (4a): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)

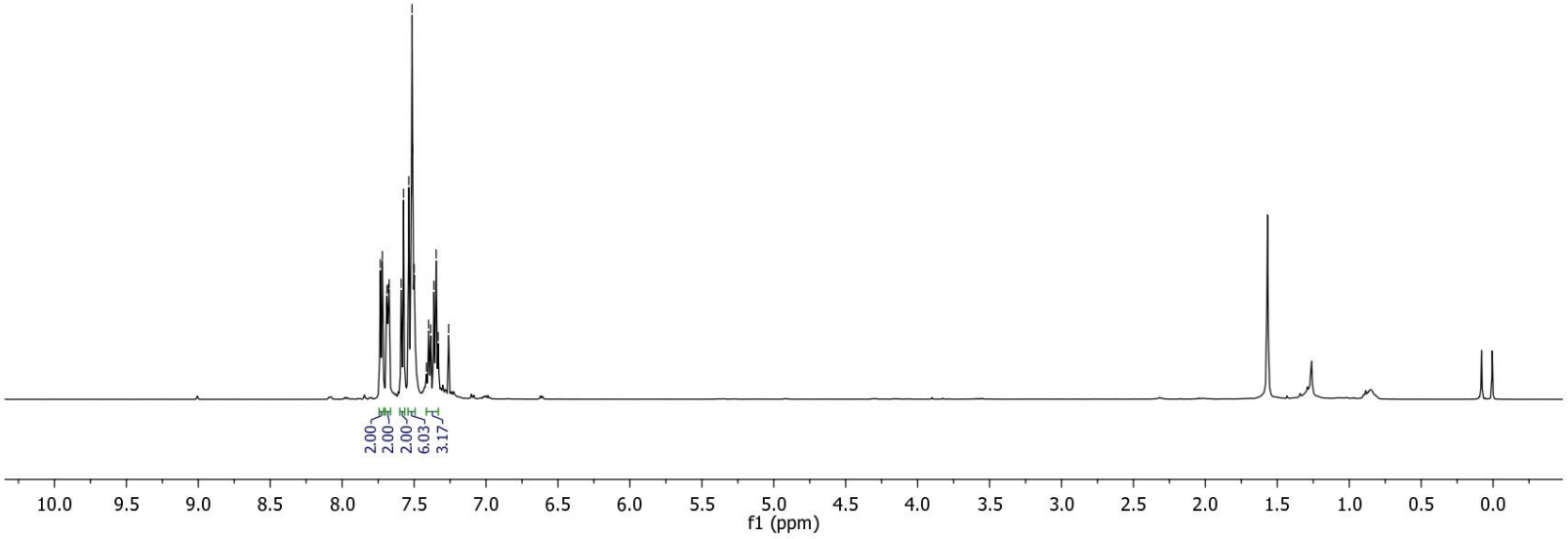


4-(4-Fluorophenyl)-6-phenyl-2-(phenylthio)nicotinonitrile (4a): ^{19}F NMR ($CDCl_3$, 471 MHz)

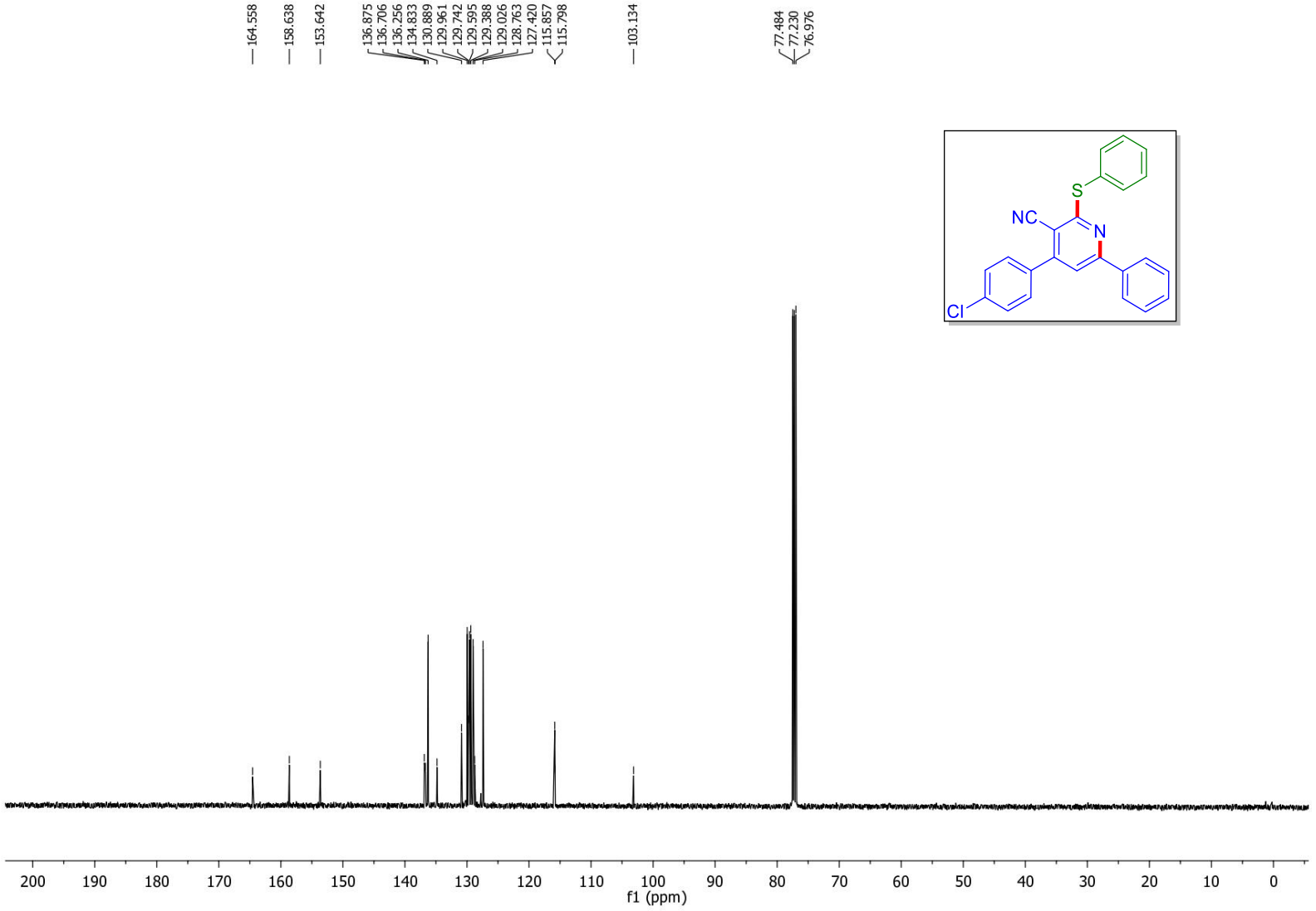


4-(4-Chlorophenyl)-6-phenyl-2-(phenylthio)nicotinonitrile (5a): ^{1}H NMR ($CDCl_3$, 500 MHz)

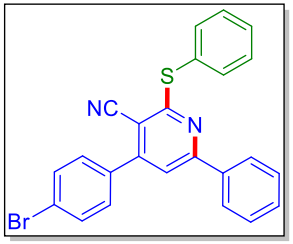


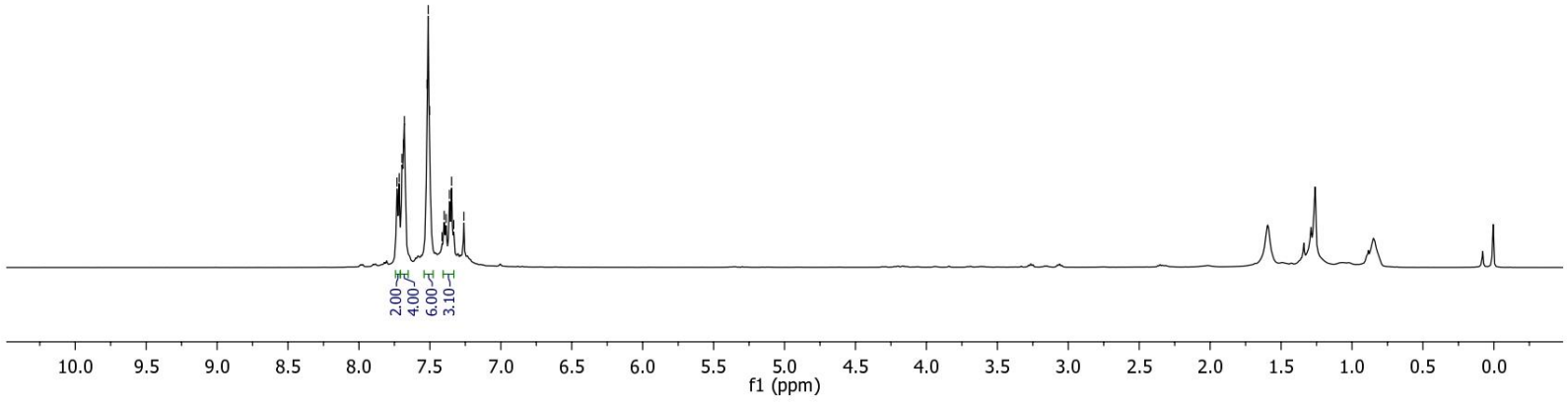


4-(4-Chlorophenyl)-6-phenyl-2-(phenylthio)nicotinonitrile (5a): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)

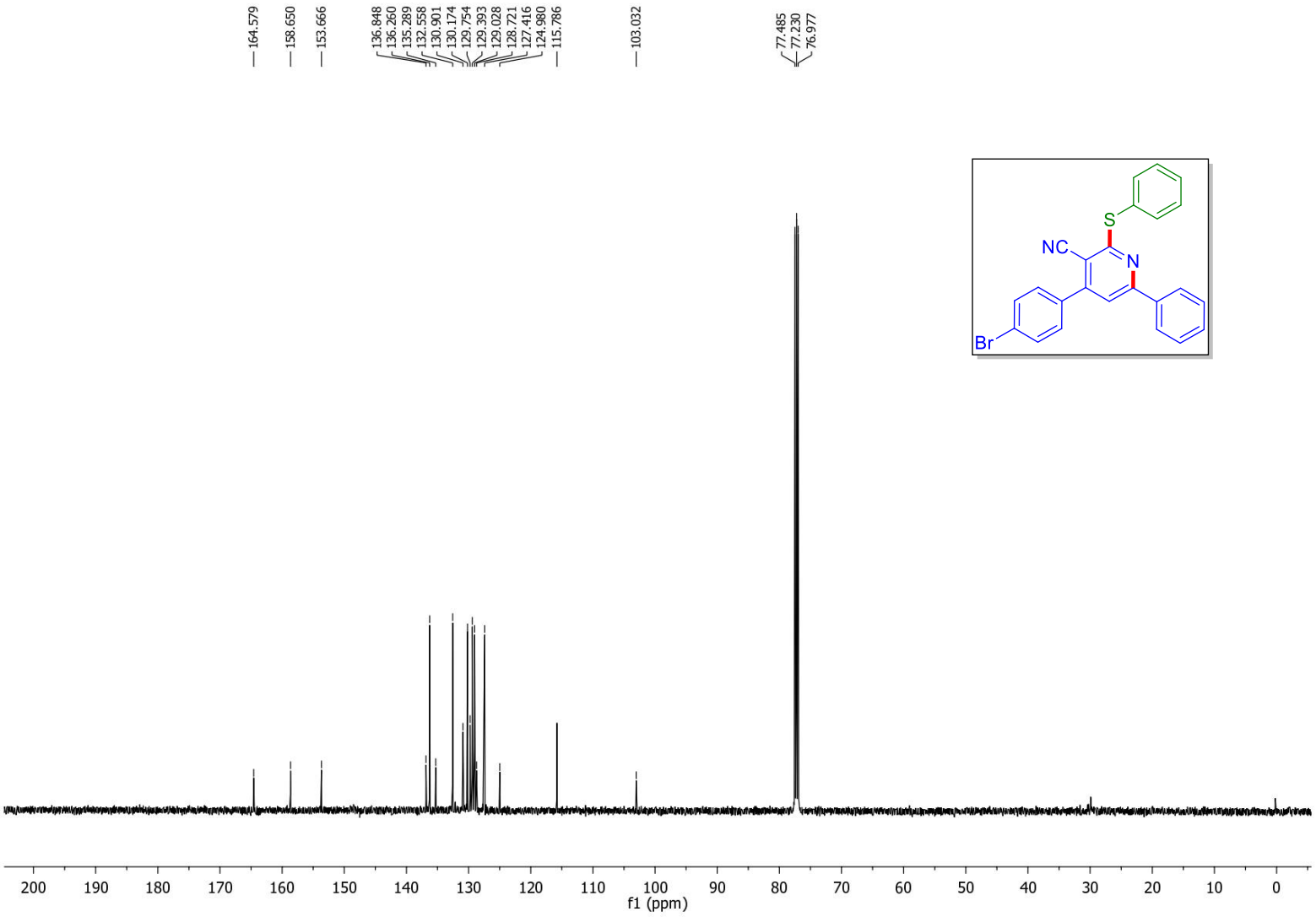


4-(4-Bromophenyl)-6-phenyl-2-(phenylthio)nicotinonitrile (6a): ^{1}H NMR ($CDCl_3$, 500 MHz)

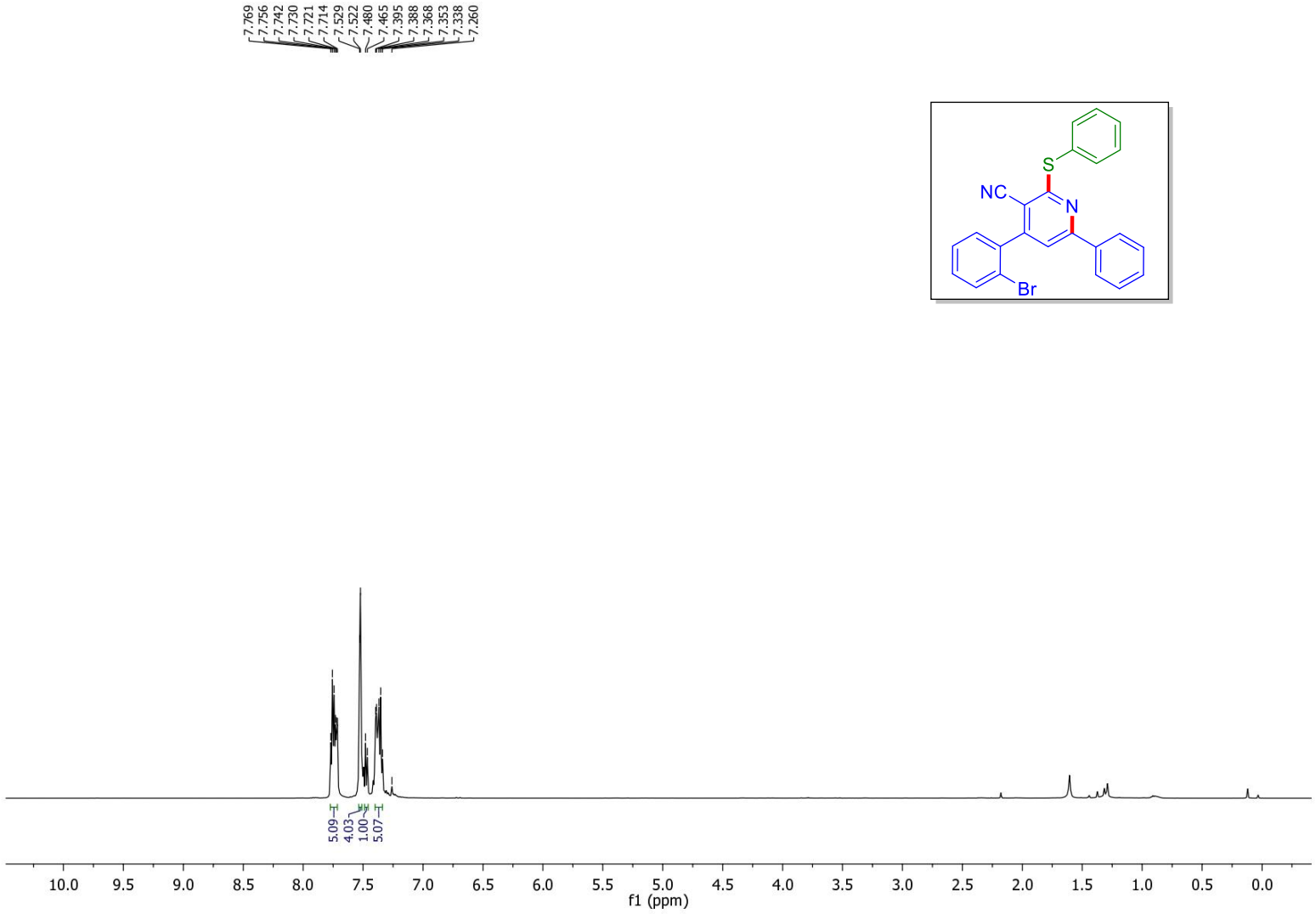




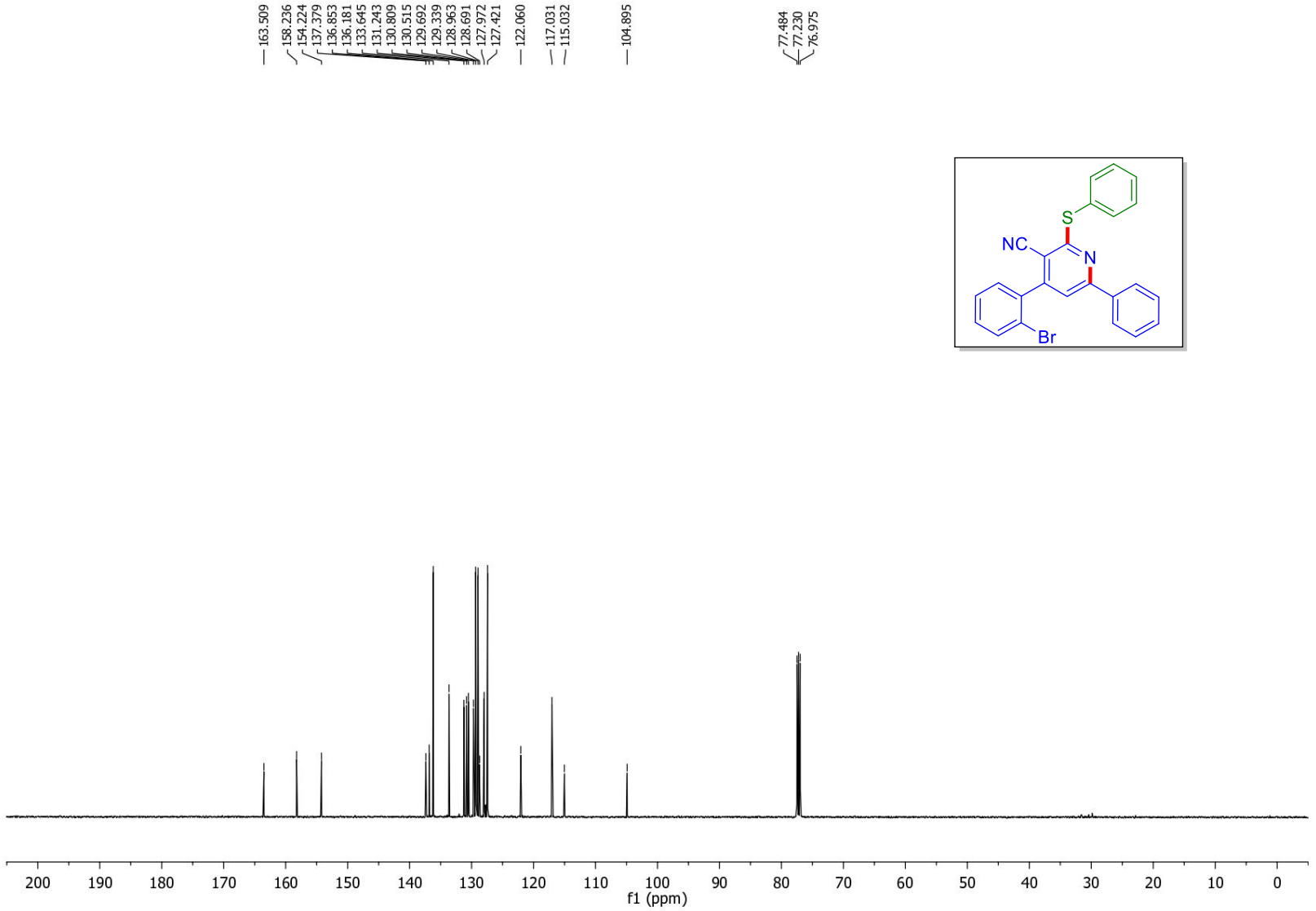
4-(4-Bromophenyl)-6-phenyl-2-(phenylthio)nicotinonitrile (6a): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



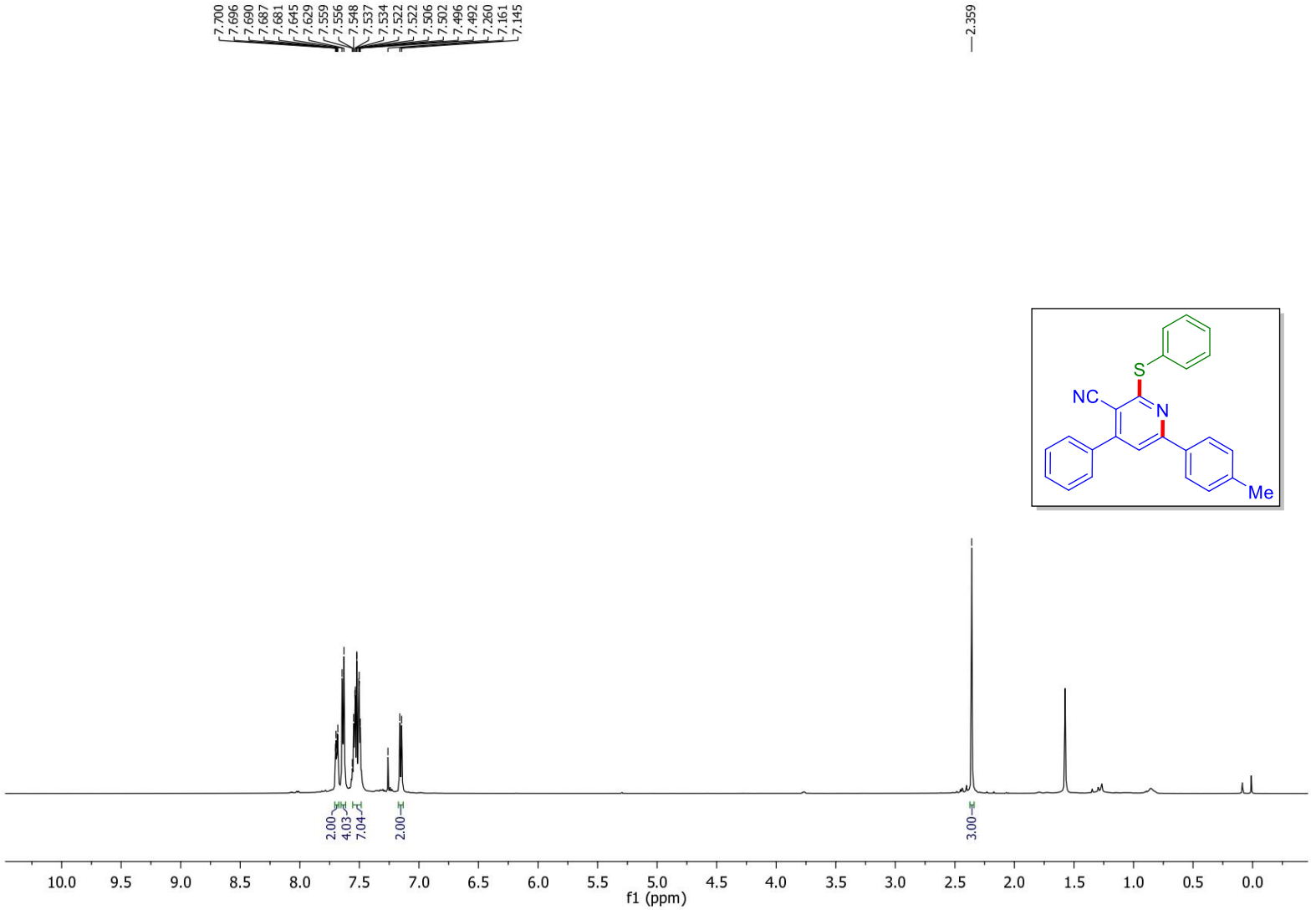
4-(2-Bromophenyl)-6-phenyl-2-(phenylthio)nicotinonitrile (7a): ^{1}H NMR ($CDCl_3$, 500 MHz)



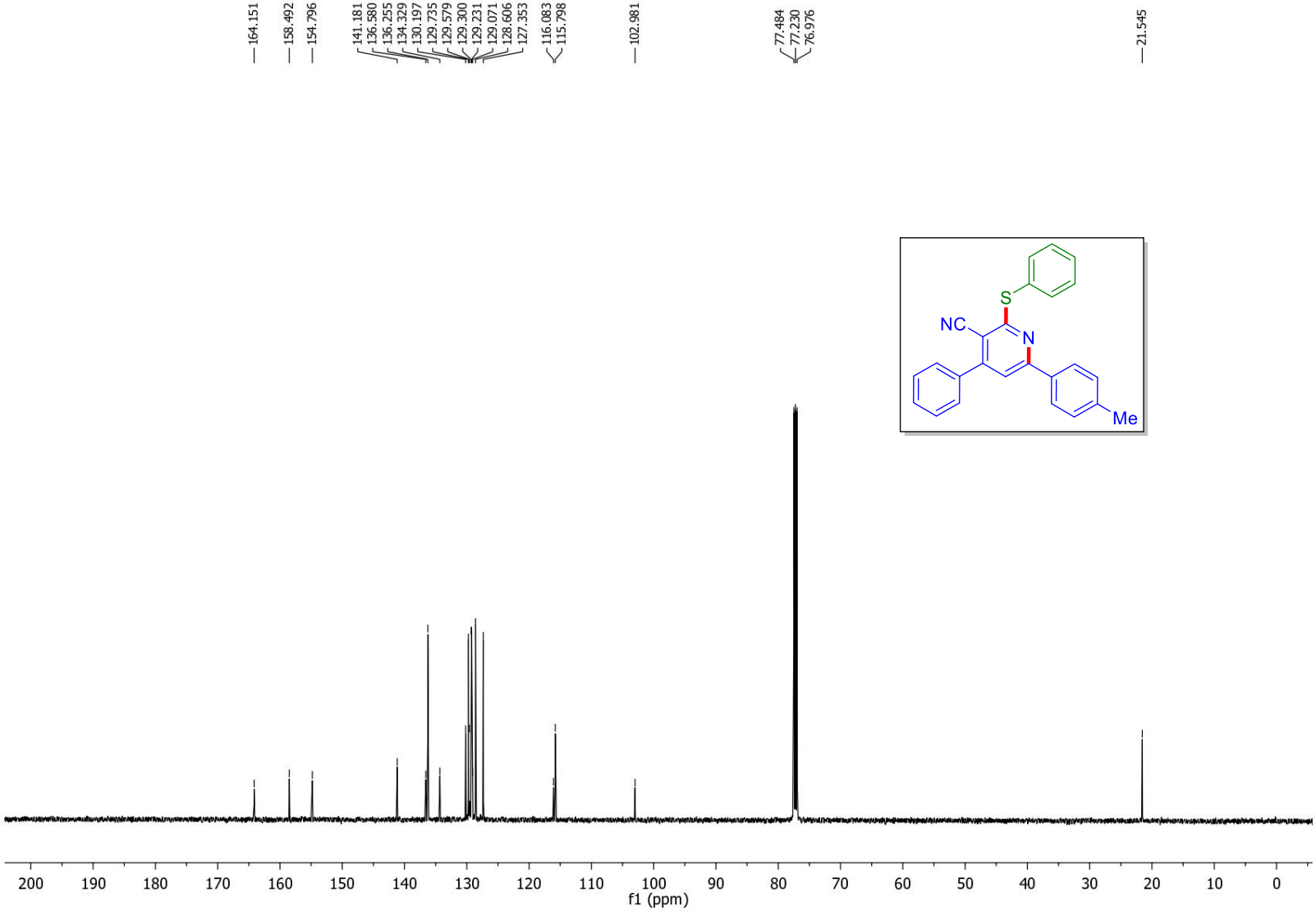
4-(2-Bromophenyl)-6-phenyl-2-(phenylthio)nicotinonitrile (7a): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



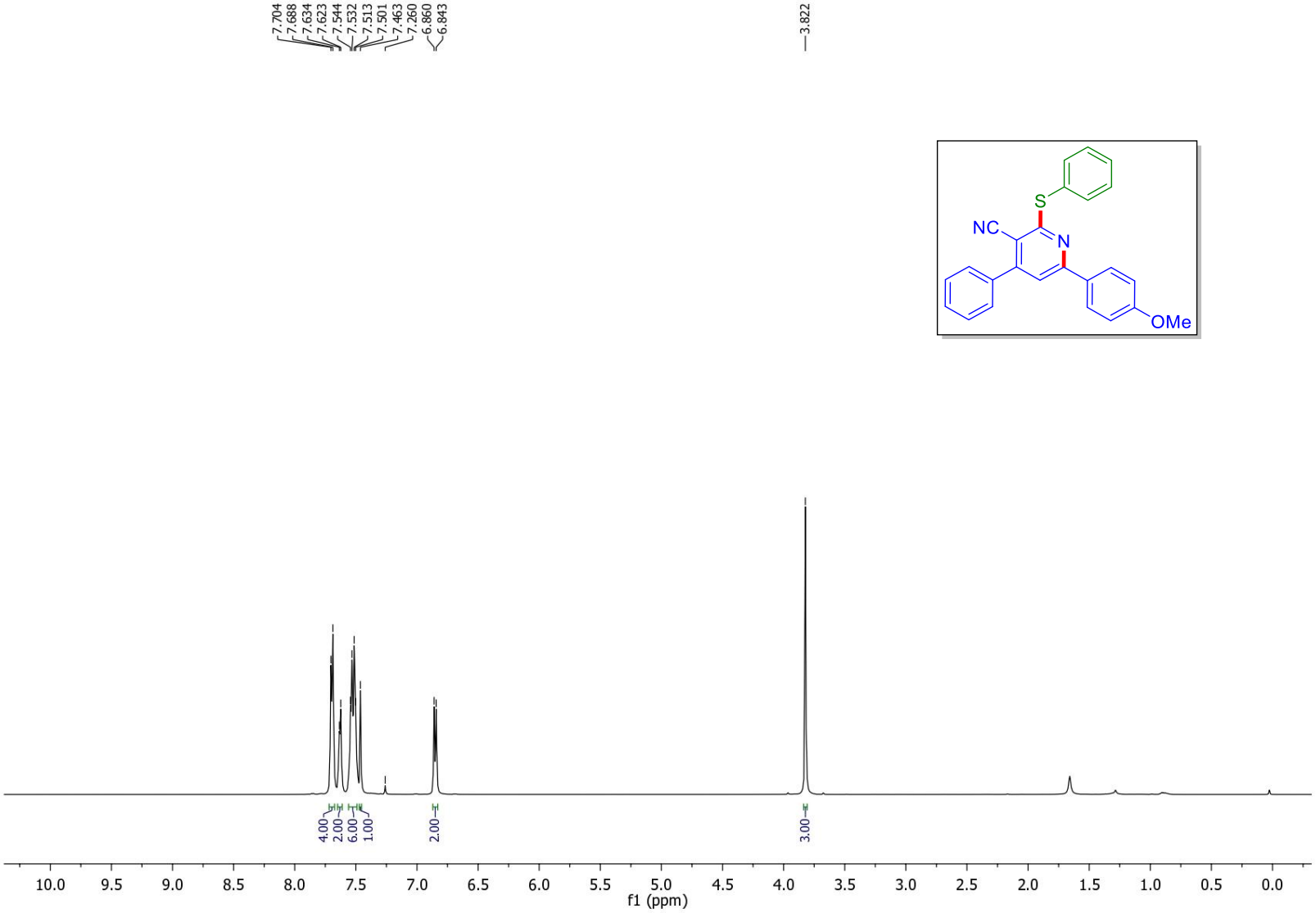
4-Phenyl-2-(phenylthio)-6-(p-tolyl)nicotinonitrile (8a): ^{1}H NMR ($CDCl_3$, 500 MHz)



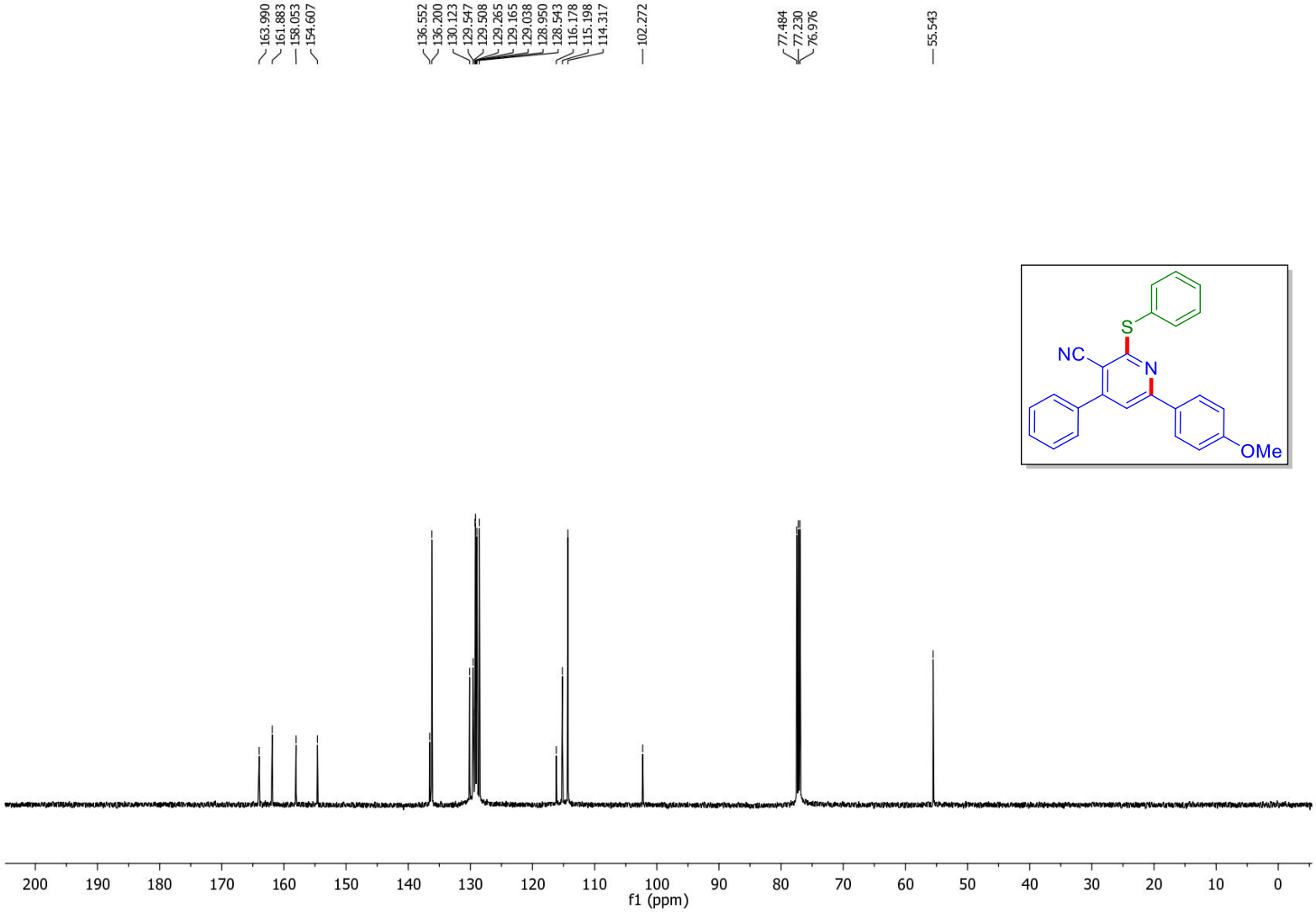
4-Phenyl-2-(phenylthio)-6-(p-tolyl)nicotinonitrile (8a): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



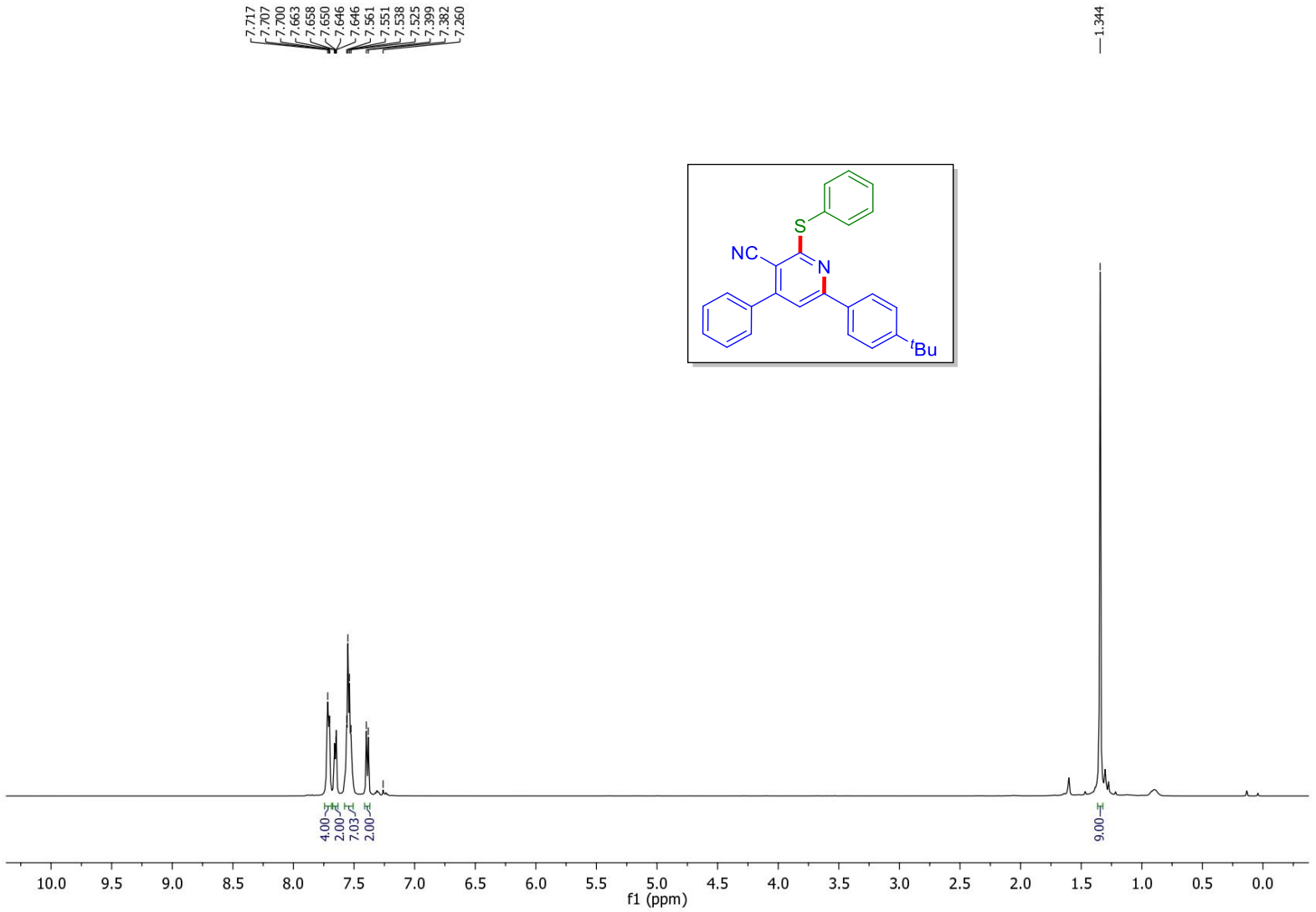
6-(4-Methoxyphenyl)-4-phenyl-2-(phenylthio)nicotinonitrile (9a): ^{1}H NMR ($CDCl_3$, 500 MHz)



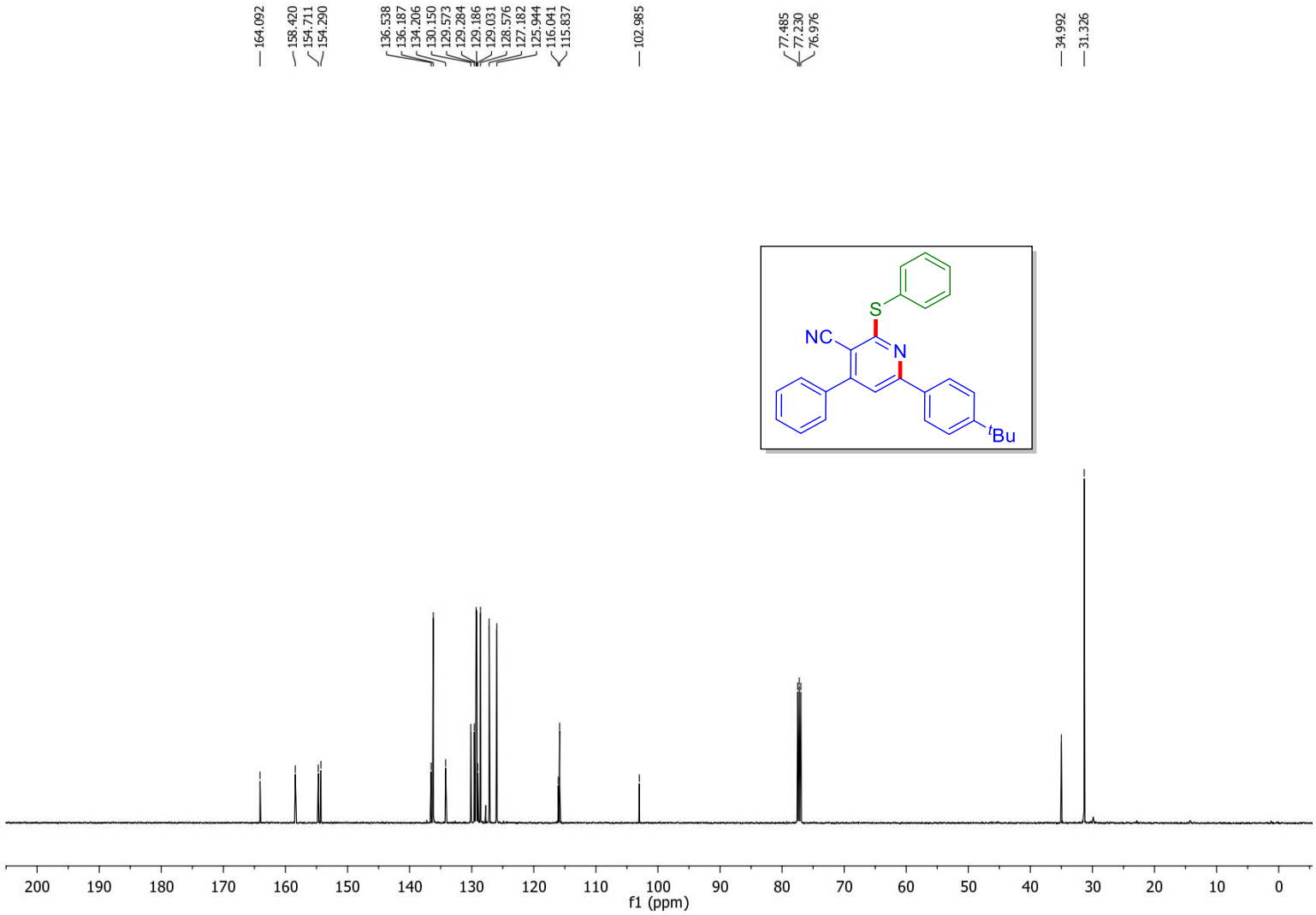
6-(4-Methoxyphenyl)-4-phenyl-2-(phenylthio)nicotinonitrile (9a): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



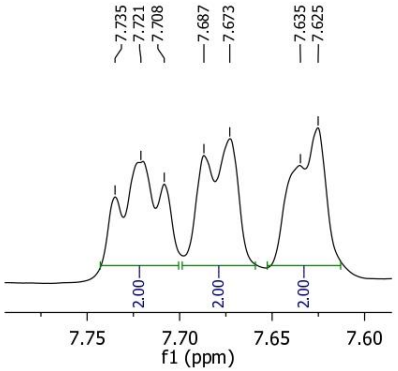
6-(4-(tert-Butyl)phenyl)-4-phenyl-2-(phenylthio)nicotinonitrile (10a): 1H NMR (CDCl3, 500 MHz)

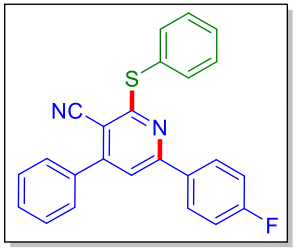


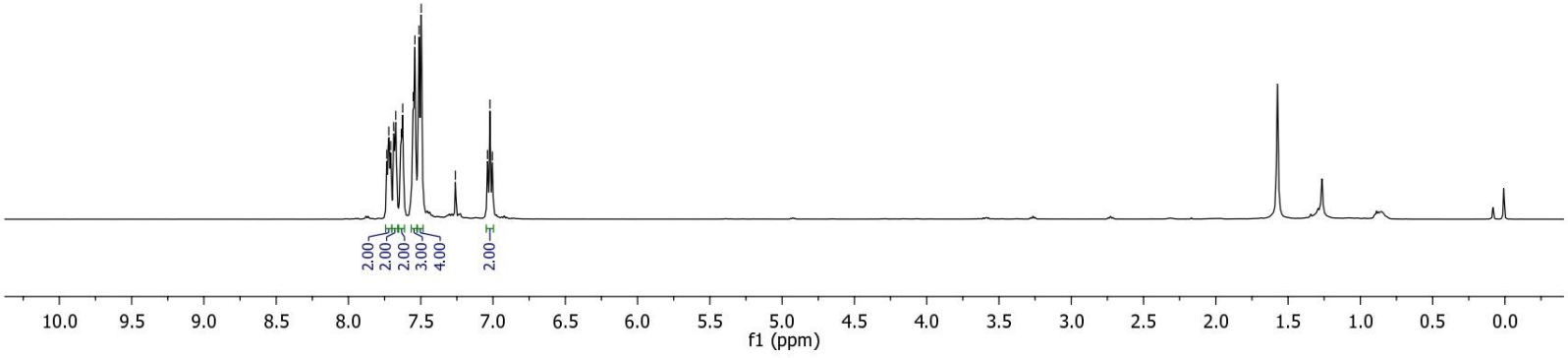
6-(4-(tert-Butyl)phenyl)-4-phenyl-2-(phenylthio)nicotinonitrile (10a): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



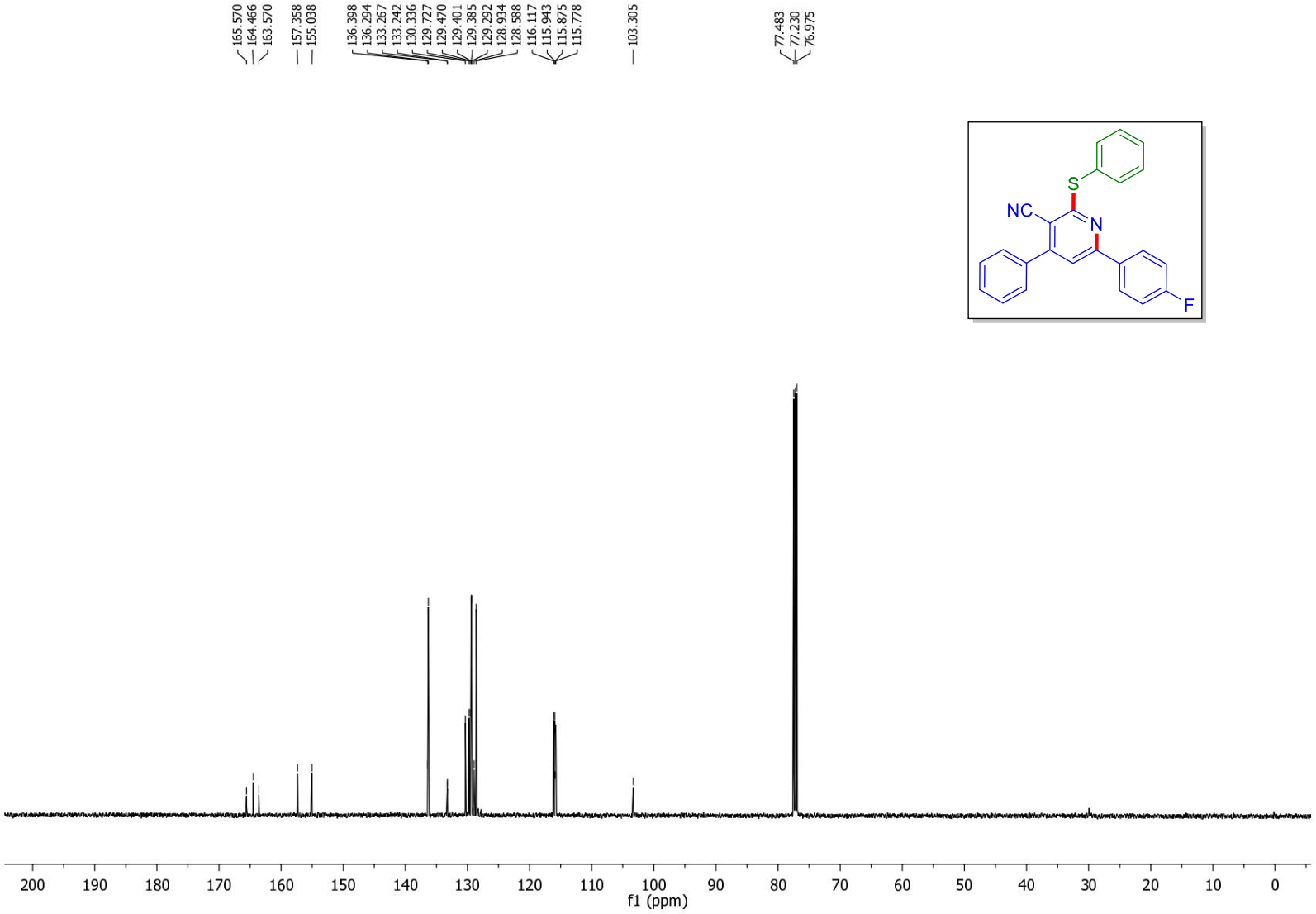
6-(4-Fluorophenyl)-4-phenyl-2-(phenylthio)nicotinonitrile (11a): ^{1}H NMR (CDCl$_3$, 500 MHz)



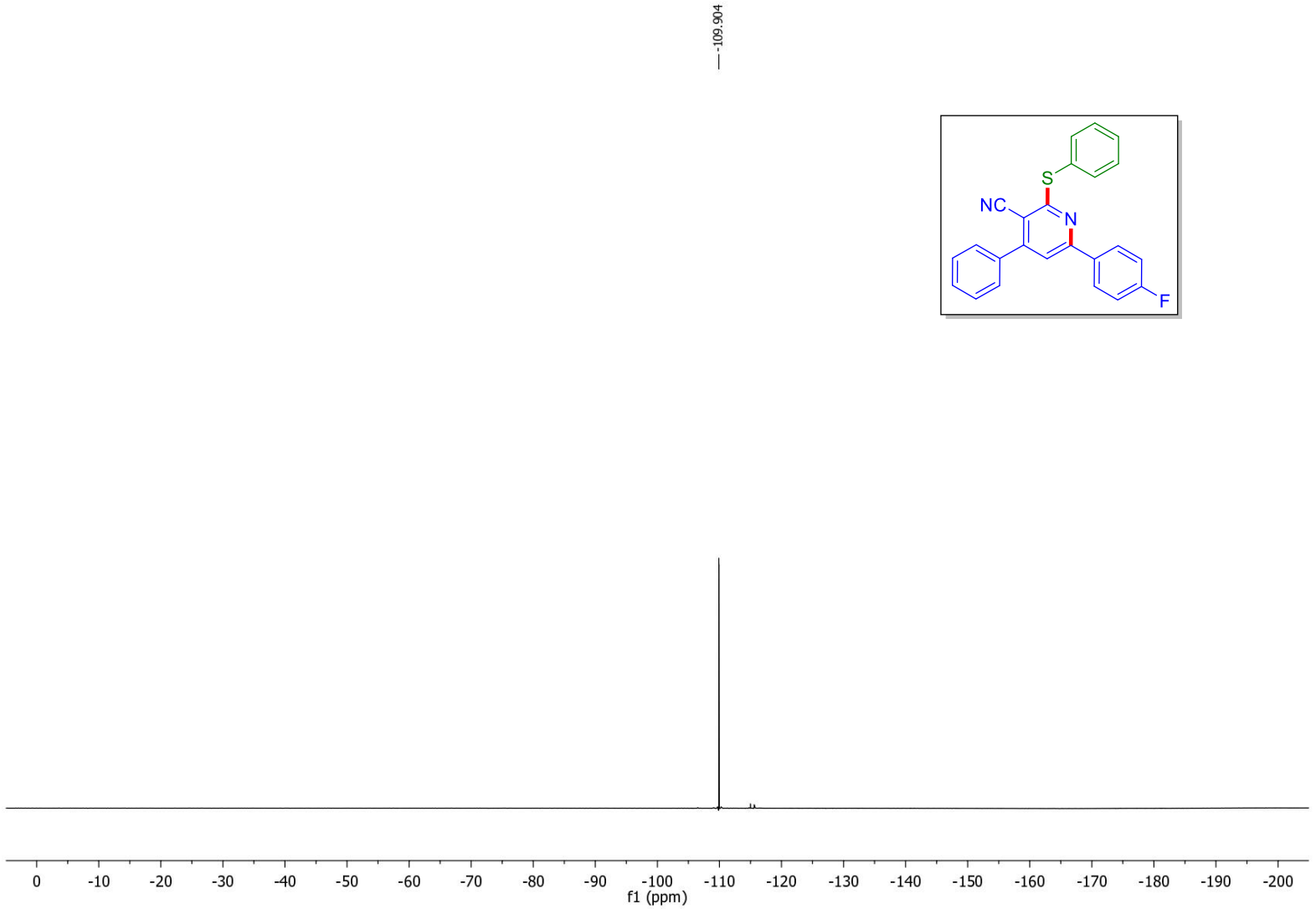




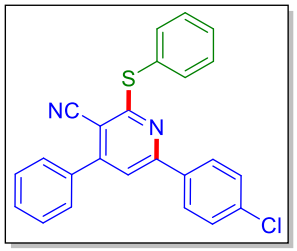
6-(4-Fluorophenyl)-4-phenyl-2-(phenylthio)nicotinonitrile (11a): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)

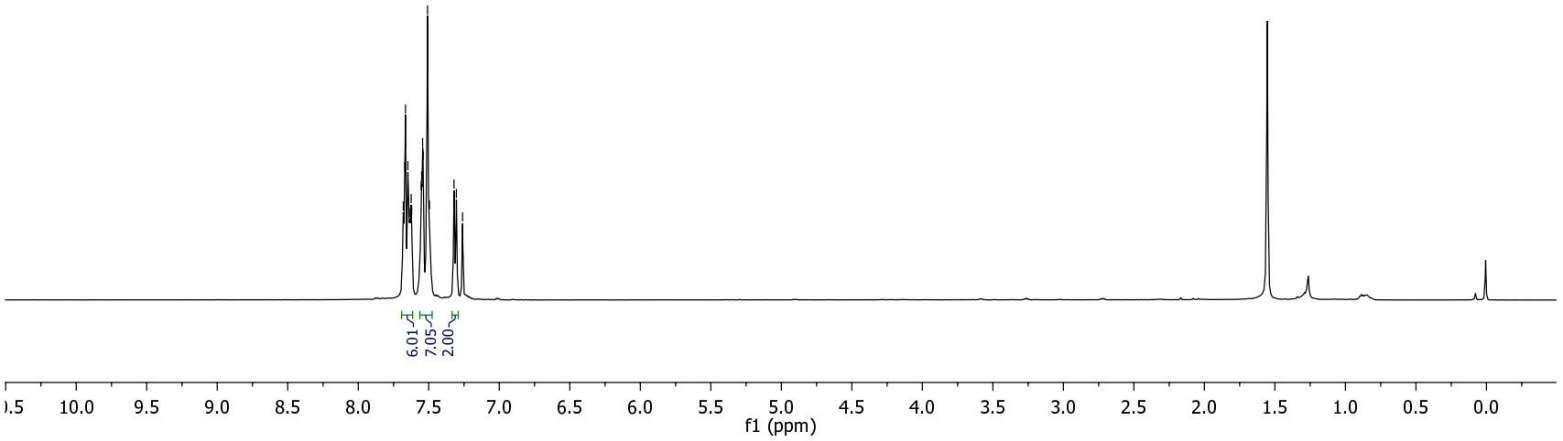


6-(4-Fluorophenyl)-4-phenyl-2-(phenylthio)nicotinonitrile (11a): ^{19}F NMR ($CDCl_3$, 471 MHz)

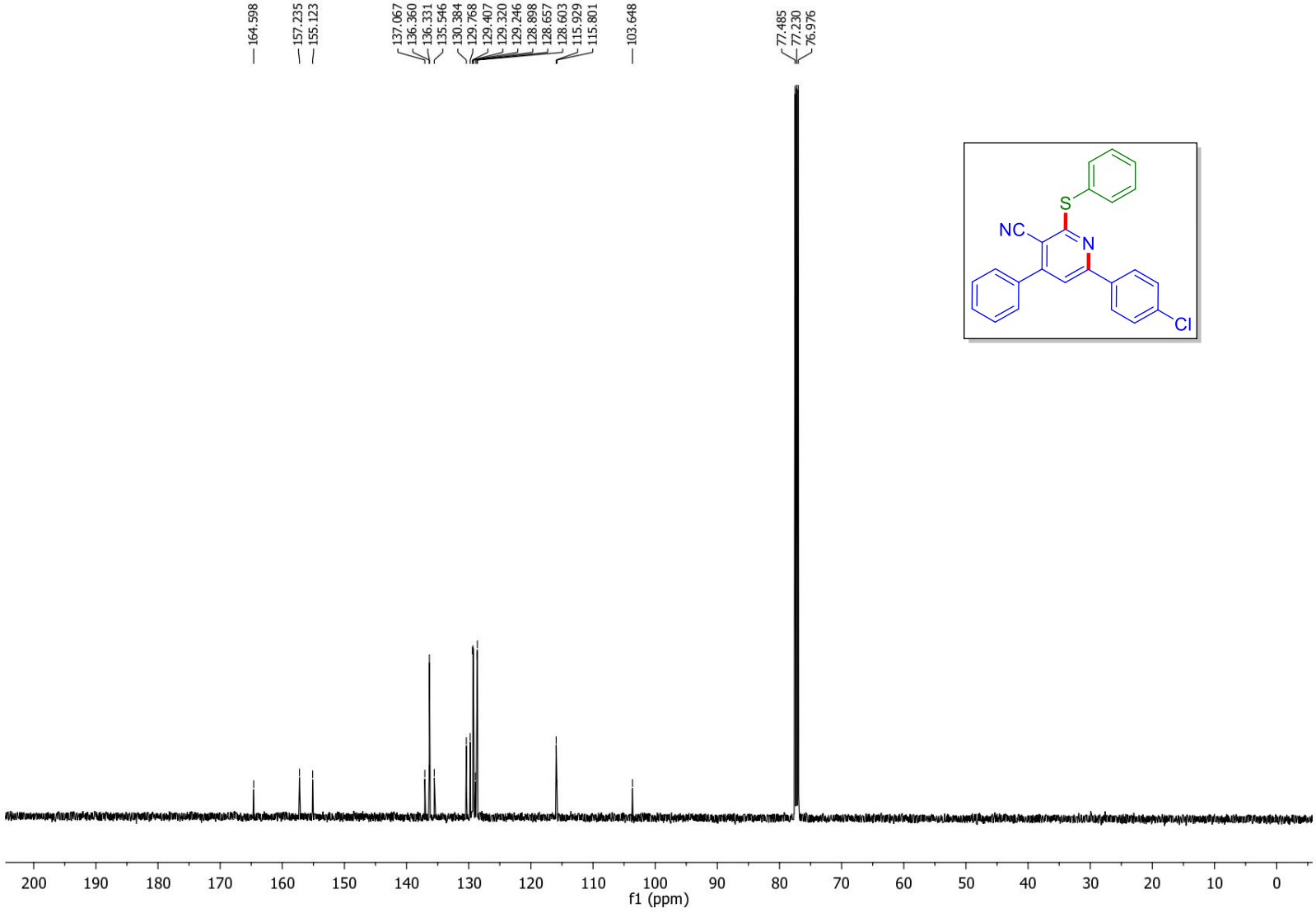


6-(4-Chlorophenyl)-4-phenyl-2-(phenylthio)nicotinonitrile (12a): ^{1}H NMR ($CDCl_3$, 500 MHz)

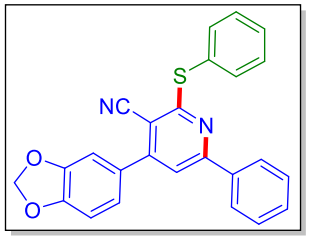


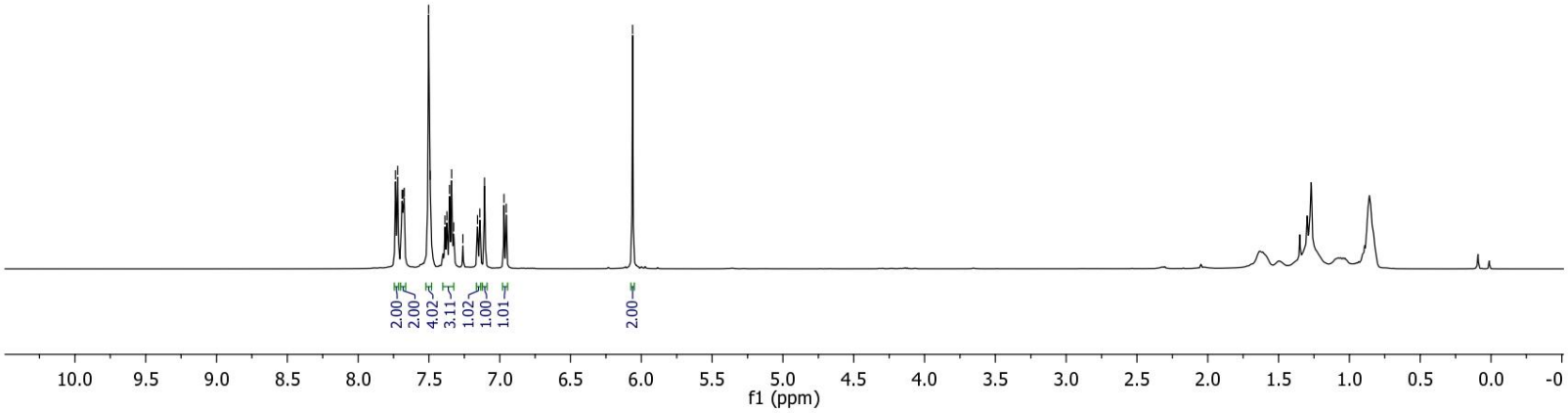


6-(4-Chlorophenyl)-4-phenyl-2-(phenylthio)nicotinonitrile (12a): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)

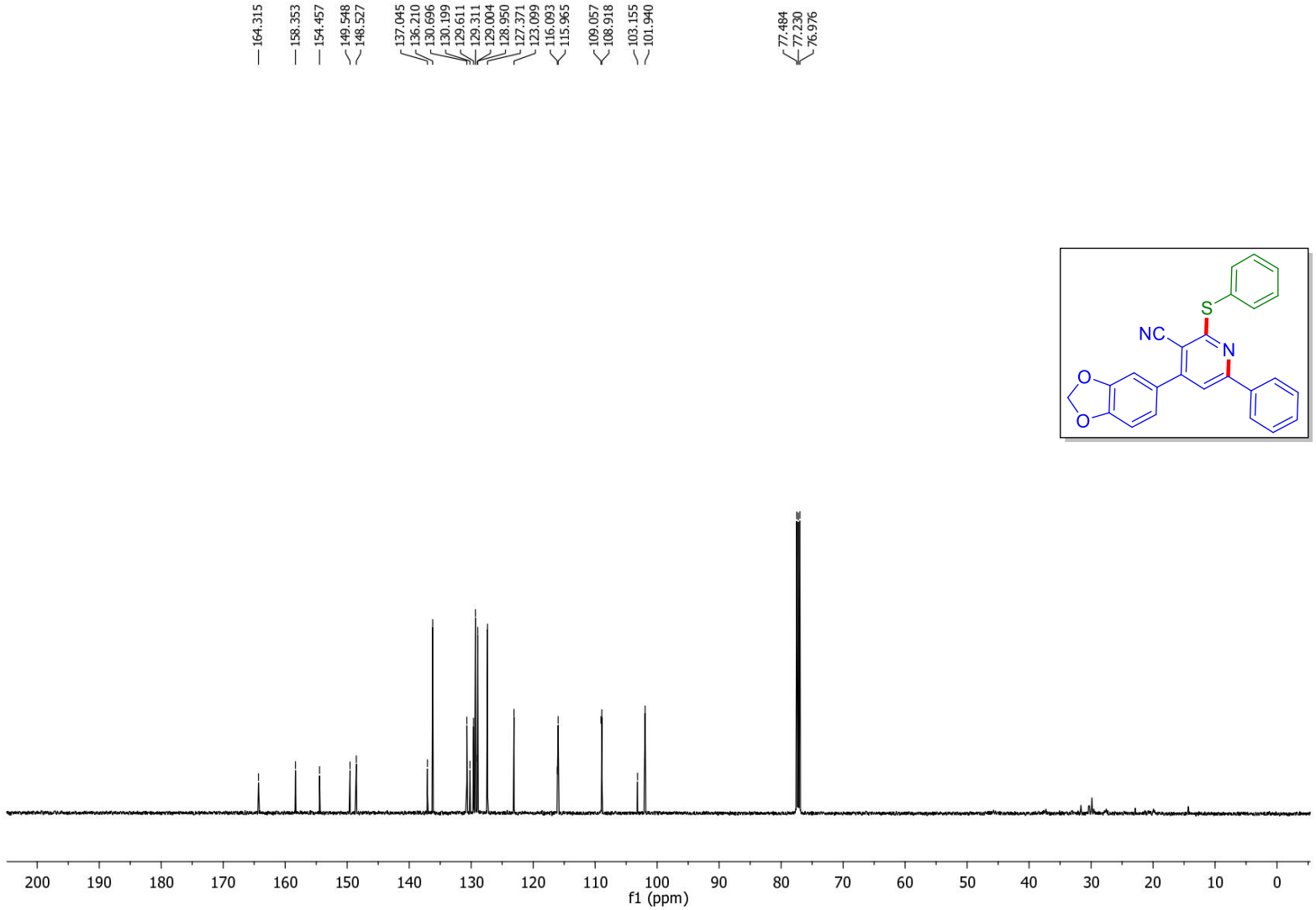


4-(Benzo[d][1,3]dioxol-5-yl)-6-phenyl-2-(phenylthio)nicotinonitrile (13a): ^{1}H NMR ($CDCl_3$, 500 MHz)

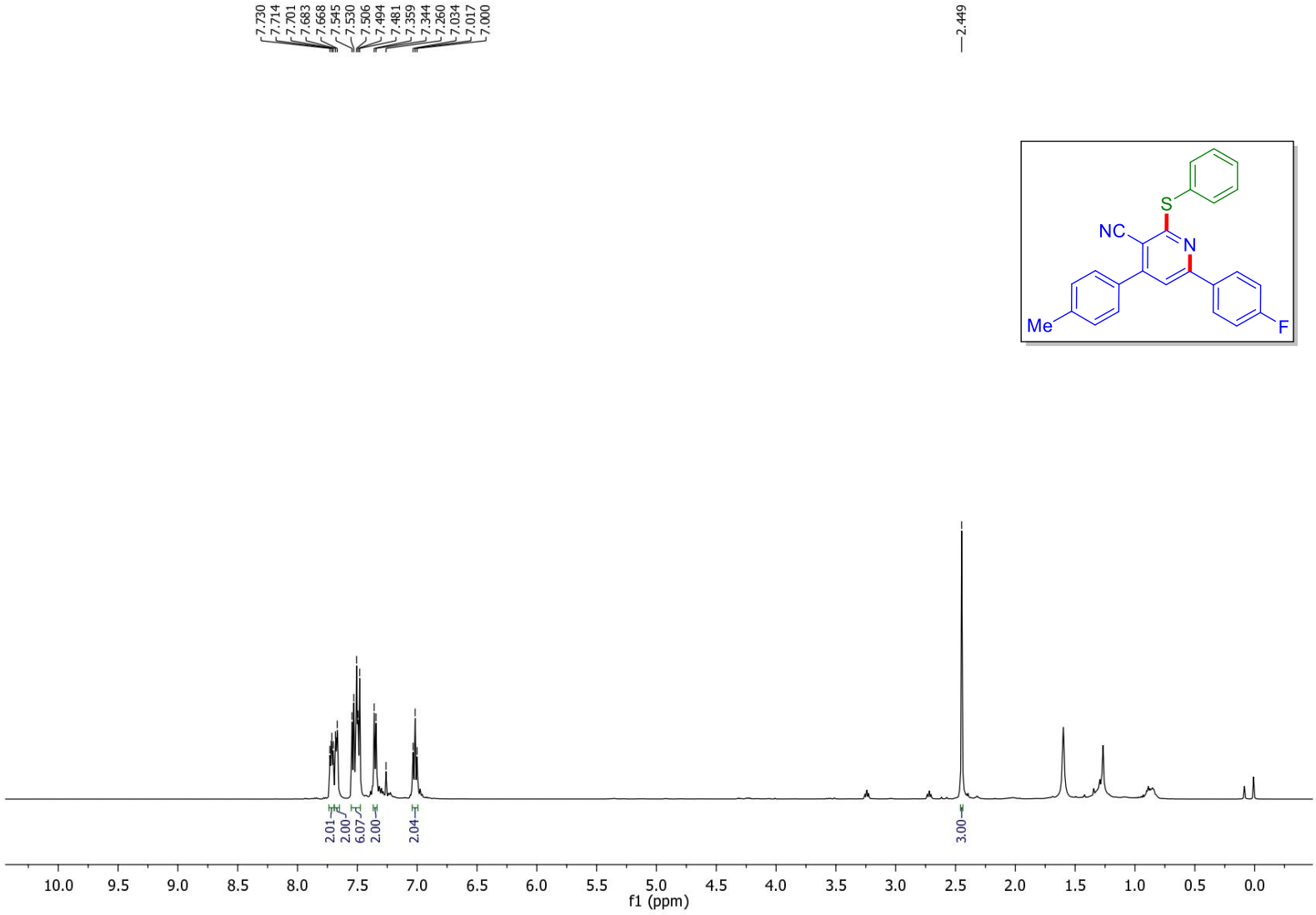




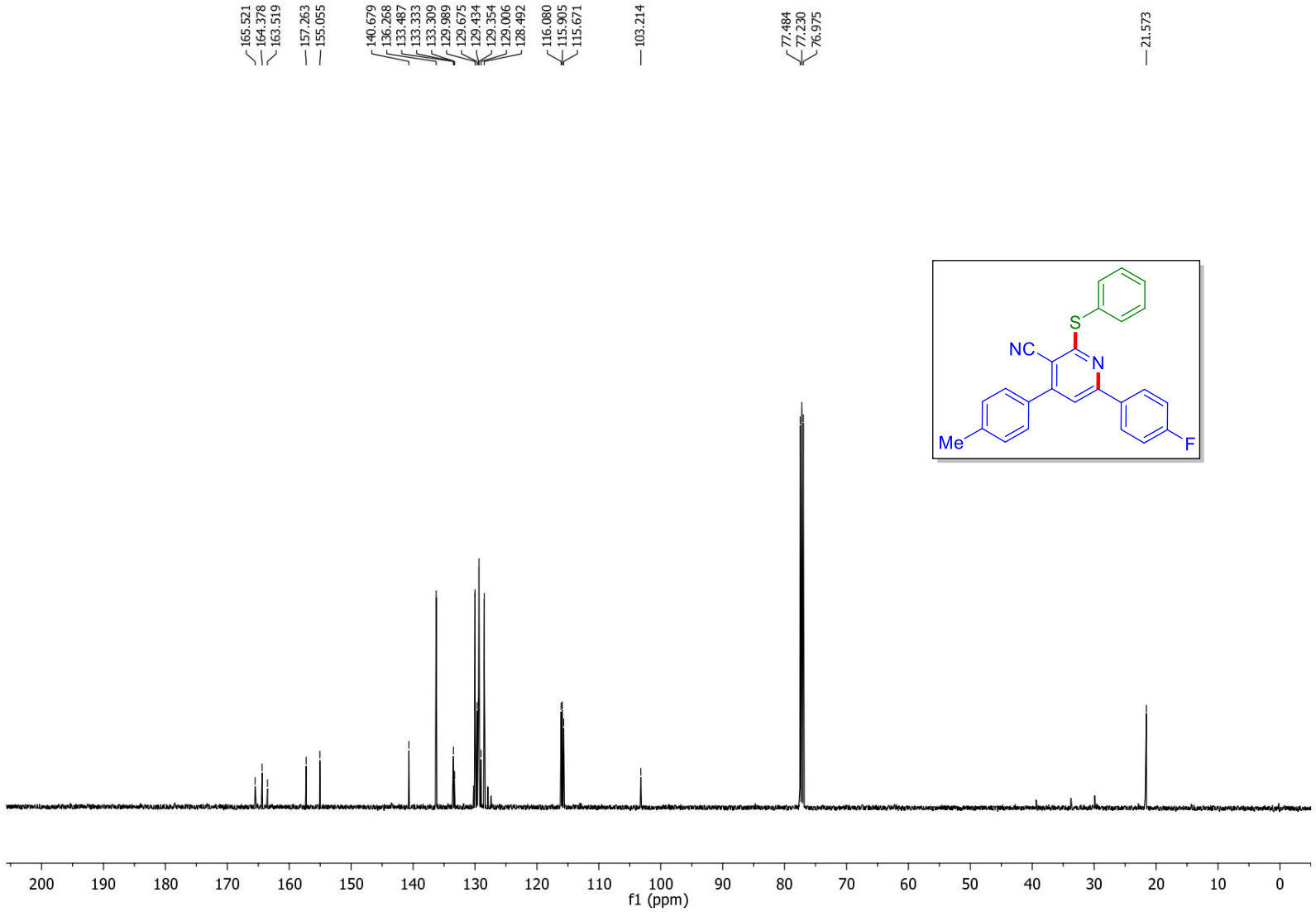
4-(Benzo[d][1,3]dioxol-5-yl)-6-phenyl-2-(phenylthio)nicotinonitrile (13a): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



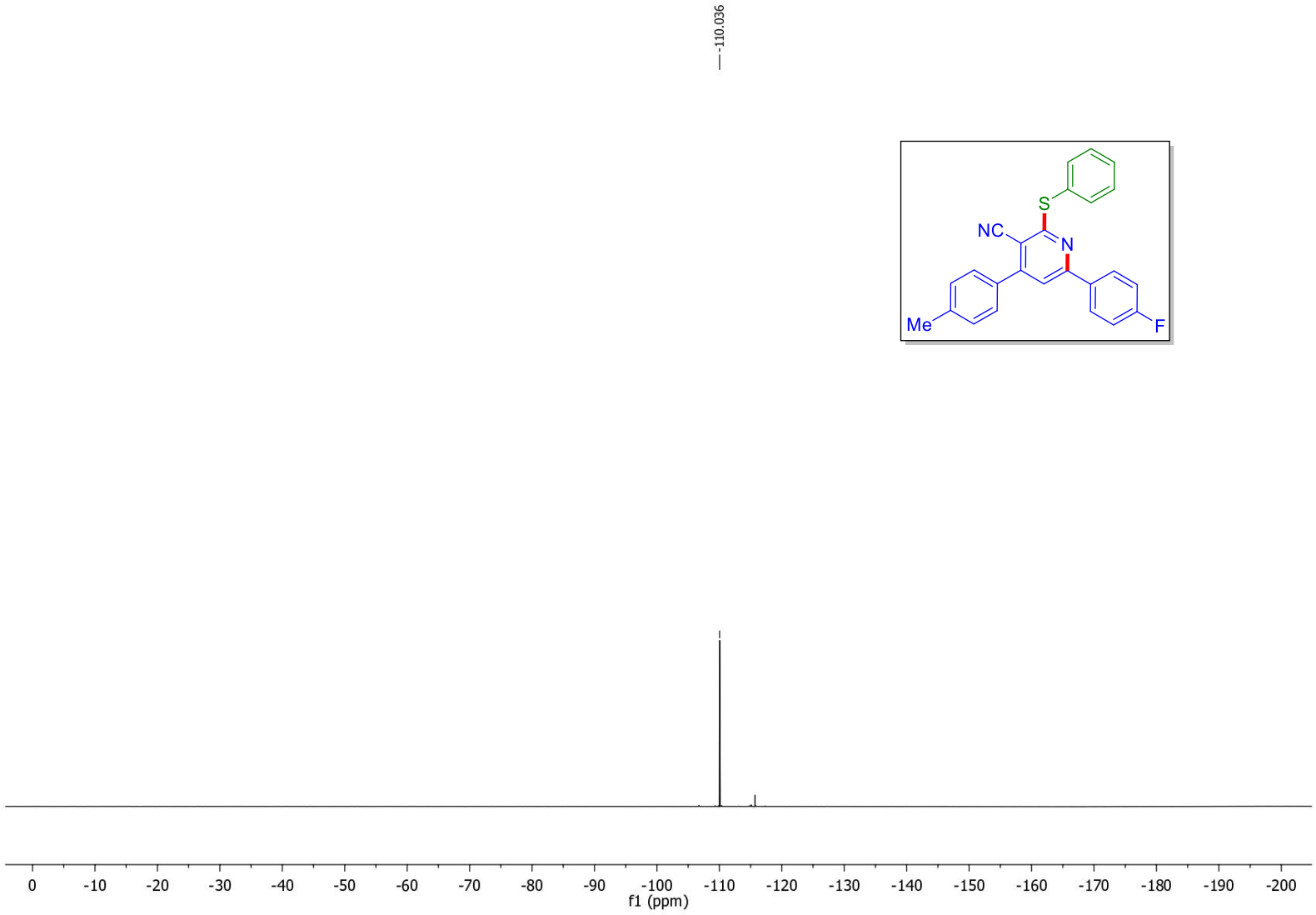
6-(4-Fluorophenyl)-2-(phenylthio)-4-(p-tolyl)nicotinonitrile (14a):^{1}H NMR ($CDCl_3$, 500 MHz)



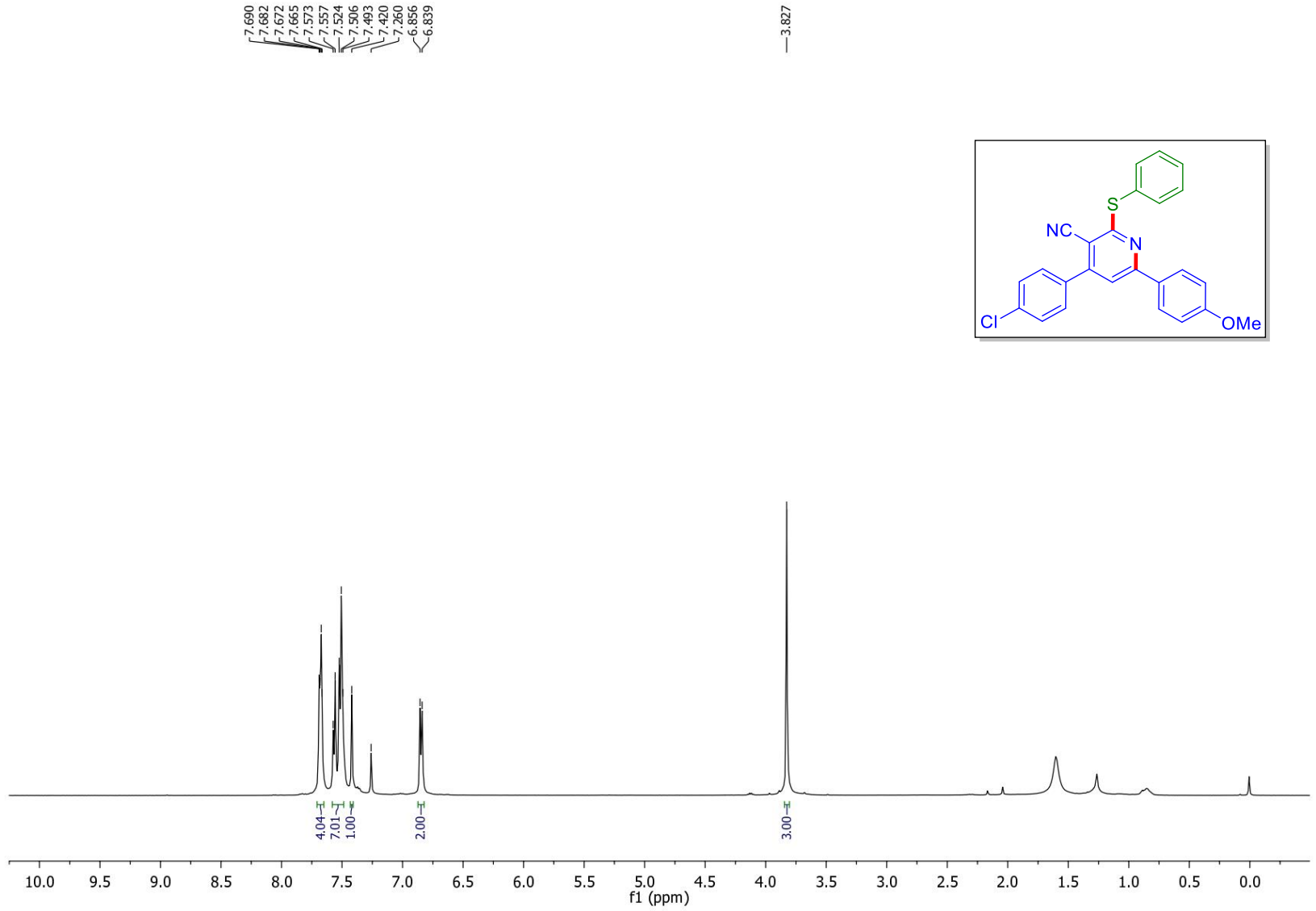
6-(4-Fluorophenyl)-2-(phenylthio)-4-(p-tolyl)nicotinonitrile (14a): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



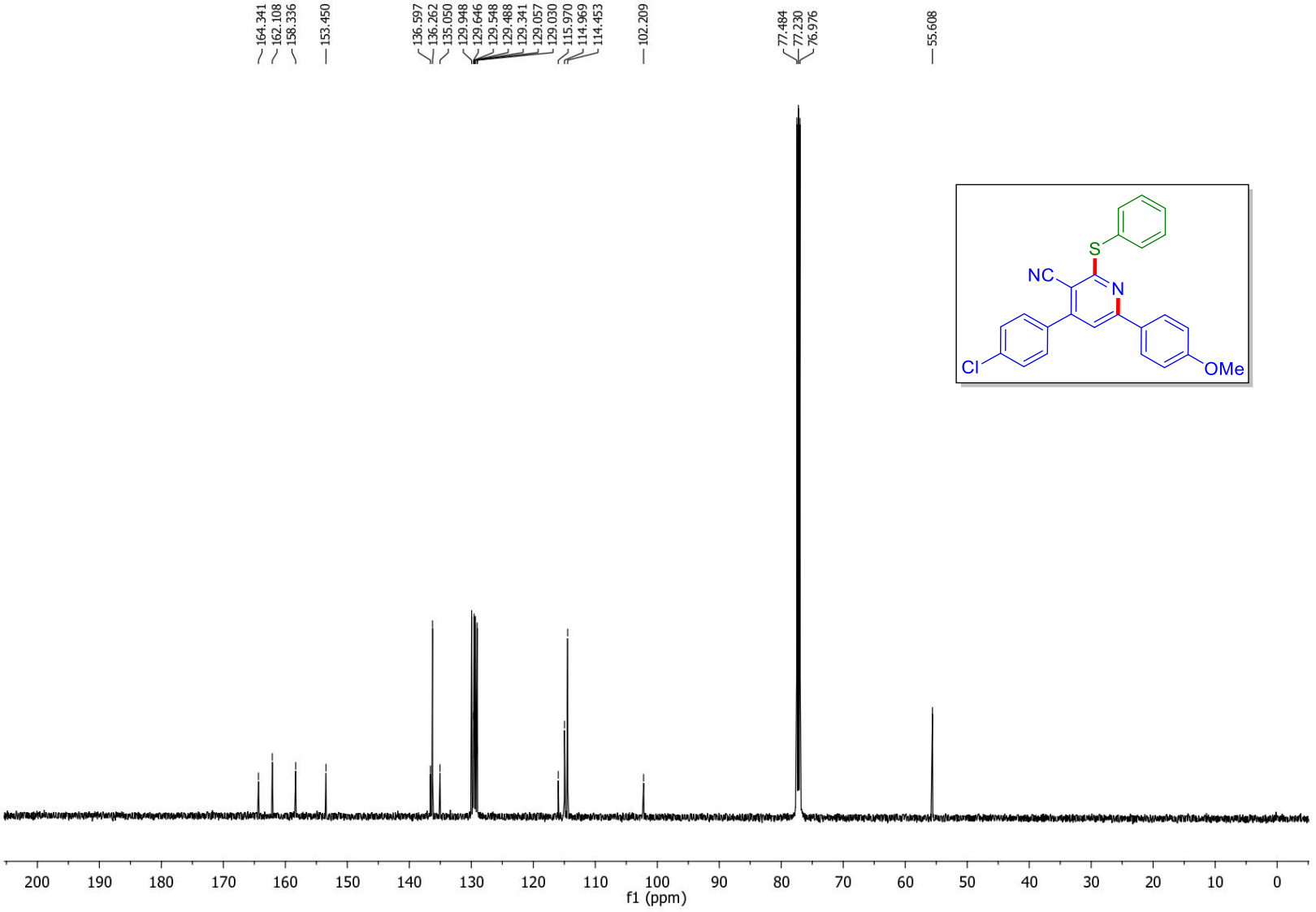
6-(4-Fluorophenyl)-2-(phenylthio)-4-(p-tolyl)nicotinonitrile (14a): ^{19}F NMR ($CDCl_3$, 471 MHz)



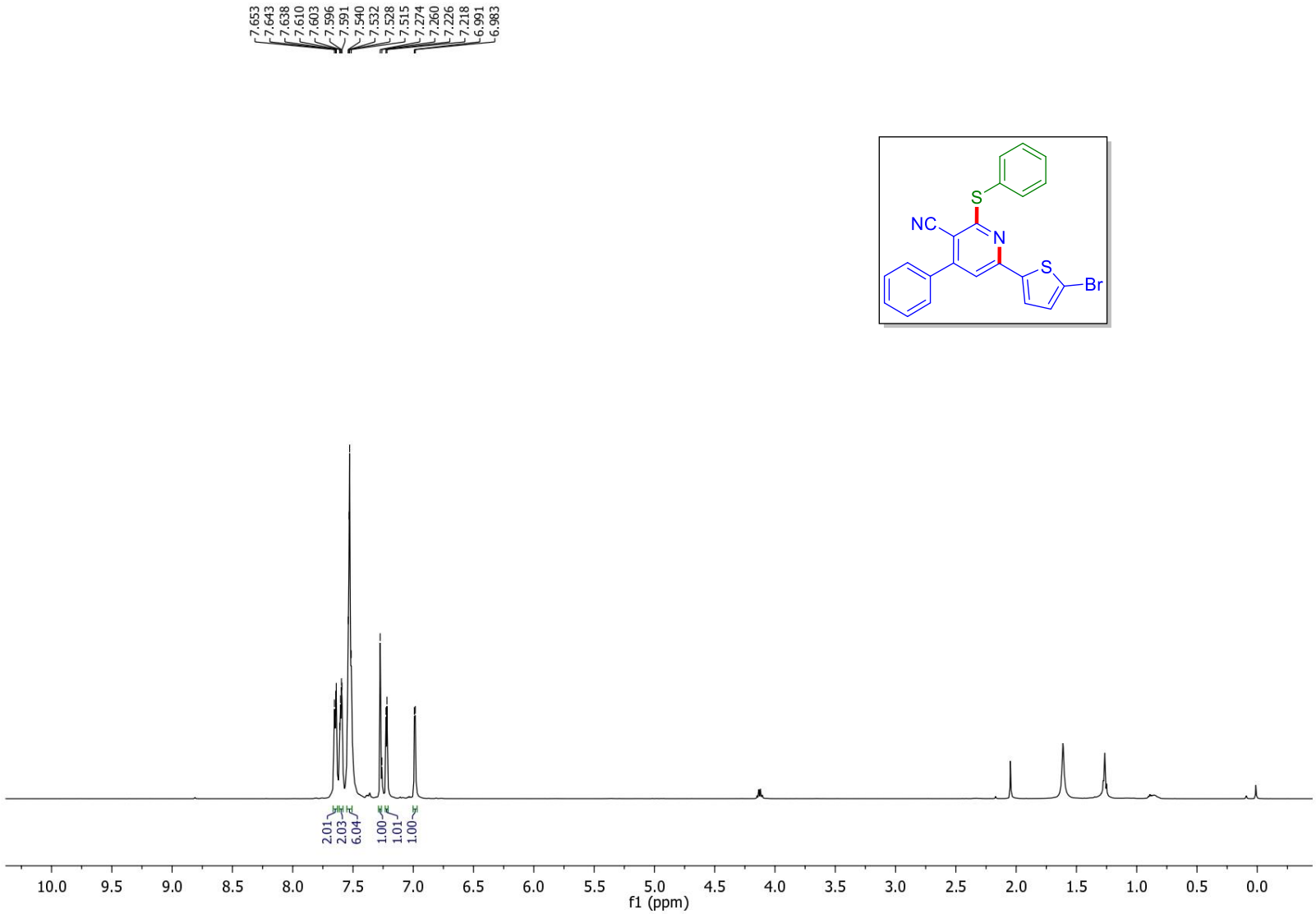
4-(4-Chlorophenyl)-6-(4-methoxyphenyl)-2-(phenylthio)nicotinonitrile (15a): ^{1}H NMR (CDCl$_3$, 500 MHz)



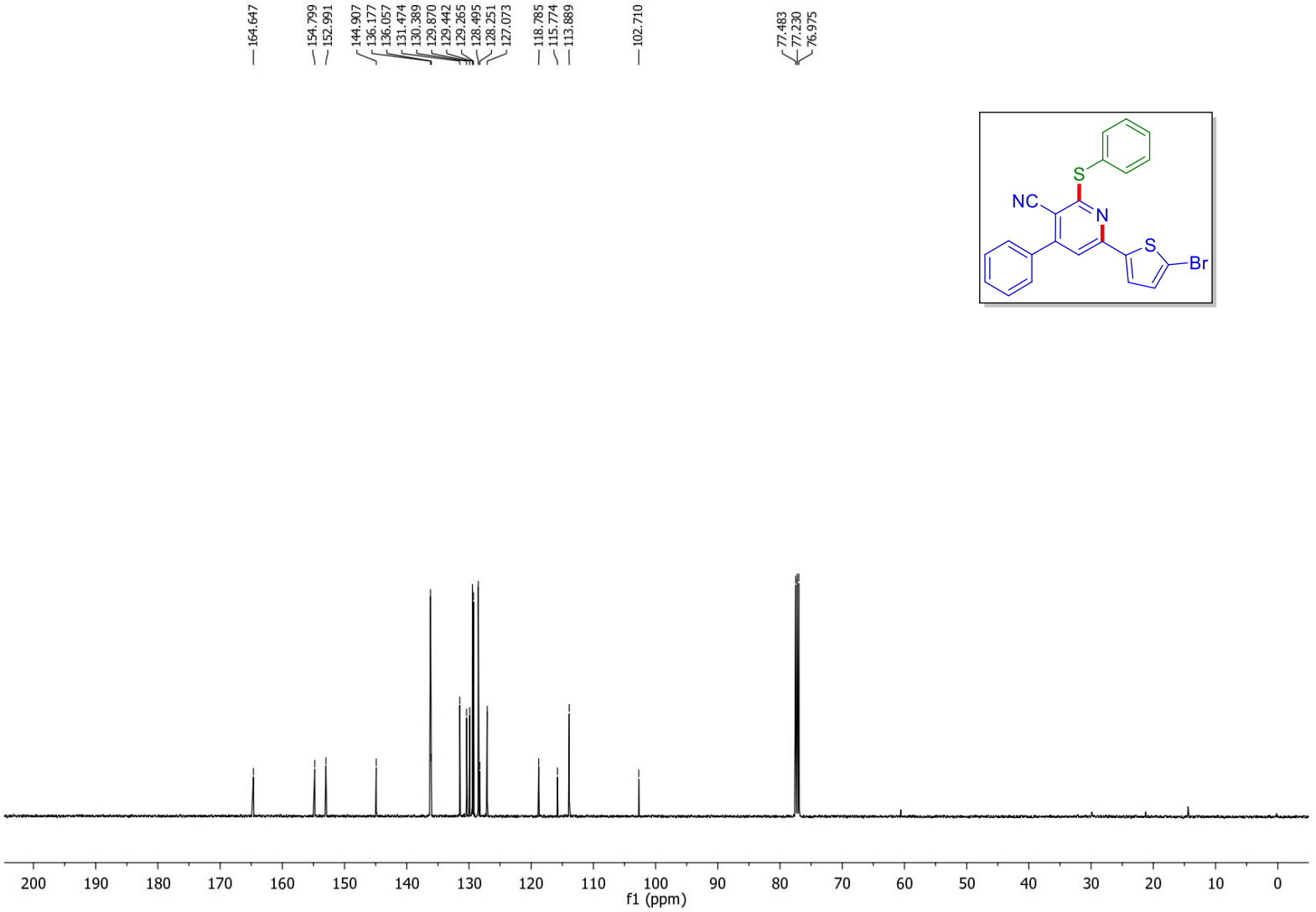
4-(4-Chlorophenyl)-6-(4-methoxyphenyl)-2-(phenylthio)nicotinonitrile (15a): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



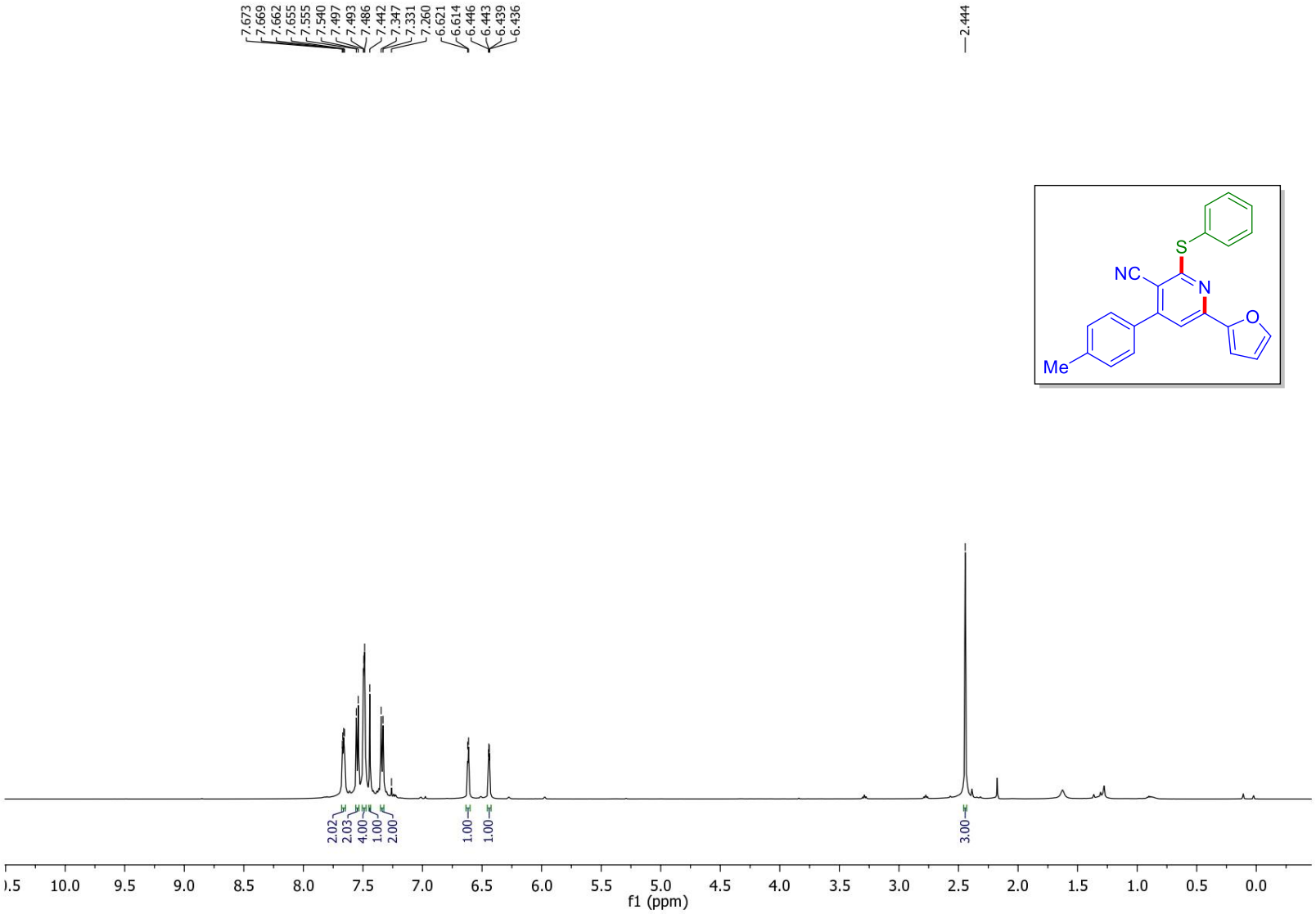
6-(5-Bromothiophen-2-yl)-4-phenyl-2-(phenylthio)nicotinonitrile (16a): ^{1}H NMR ($CDCl_3$, 500 MHz)



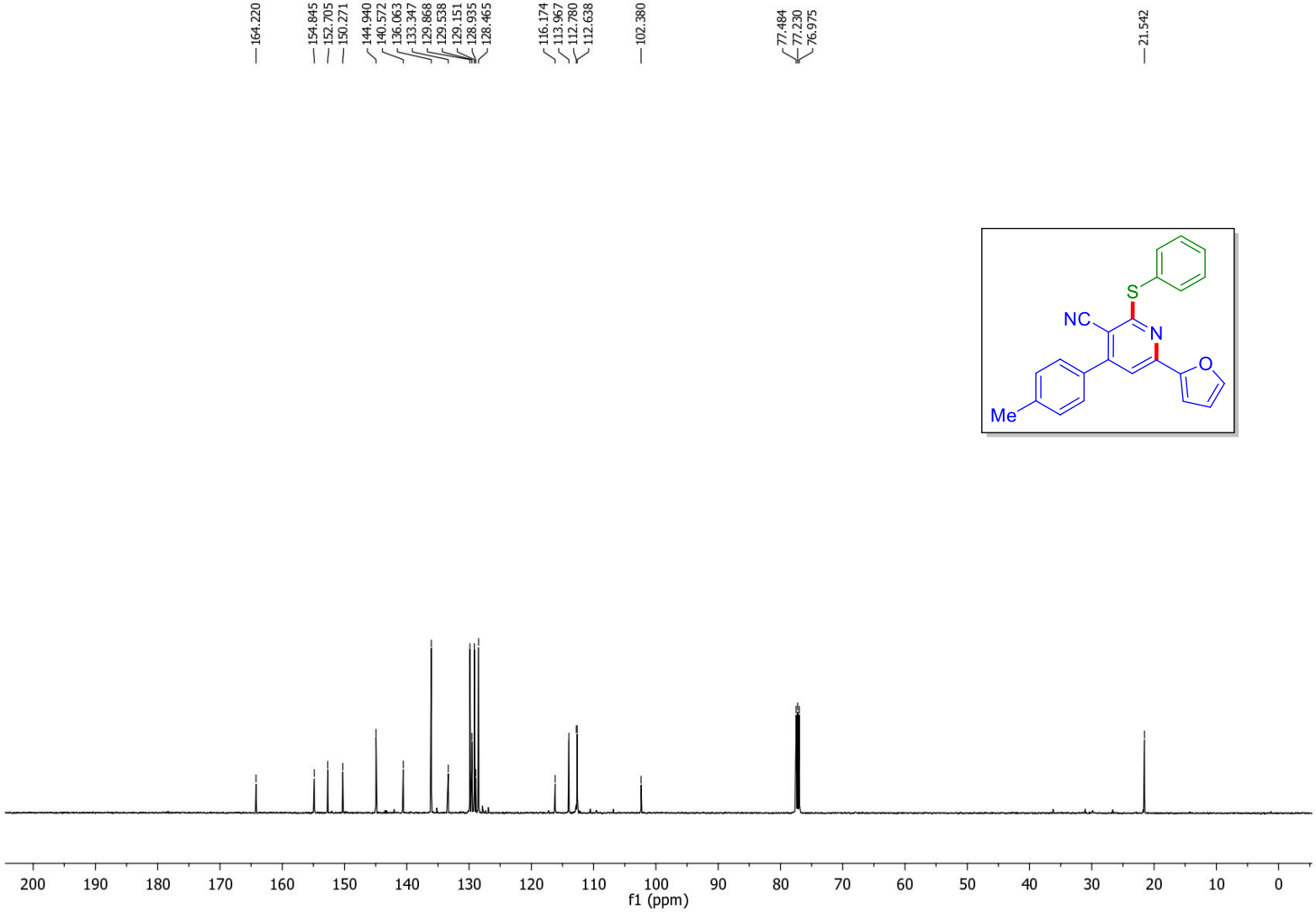
6-(5-Bromothiophen-2-yl)-4-phenyl-2-(phenylthio)nicotinonitrile (16a): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



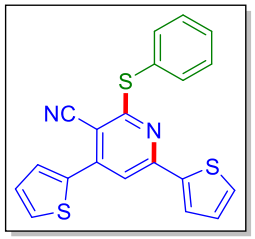
6-(Furan-2-yl)-2-(phenylthio)-4-(p-tolyl)nicotinonitrile (17a): ^{1}H NMR ($CDCl_3$, 500 MHz)

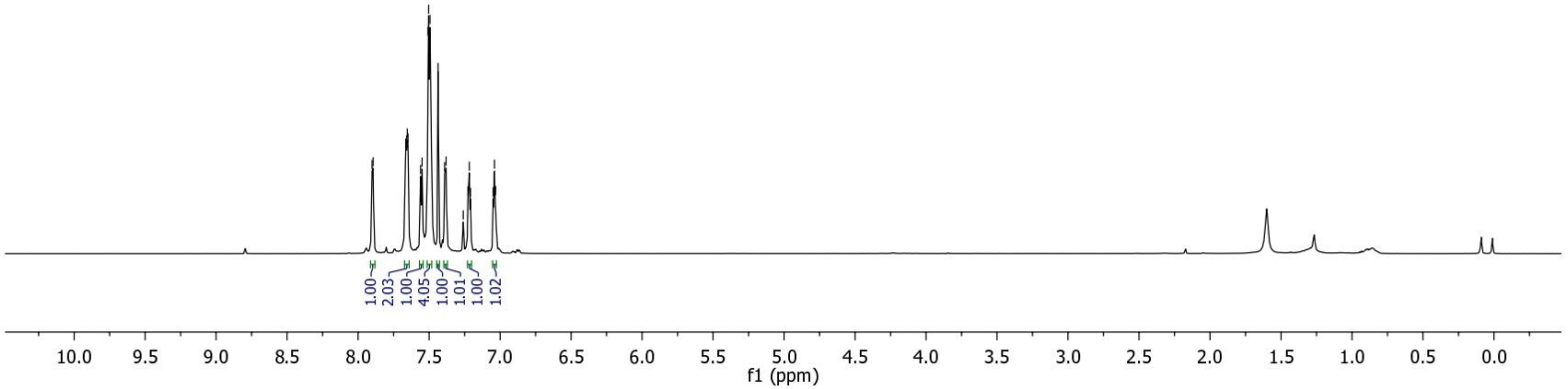


6-(Furan-2-yl)-2-(phenylthio)-4-(p-tolyl)nicotinonitrile (17a): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)

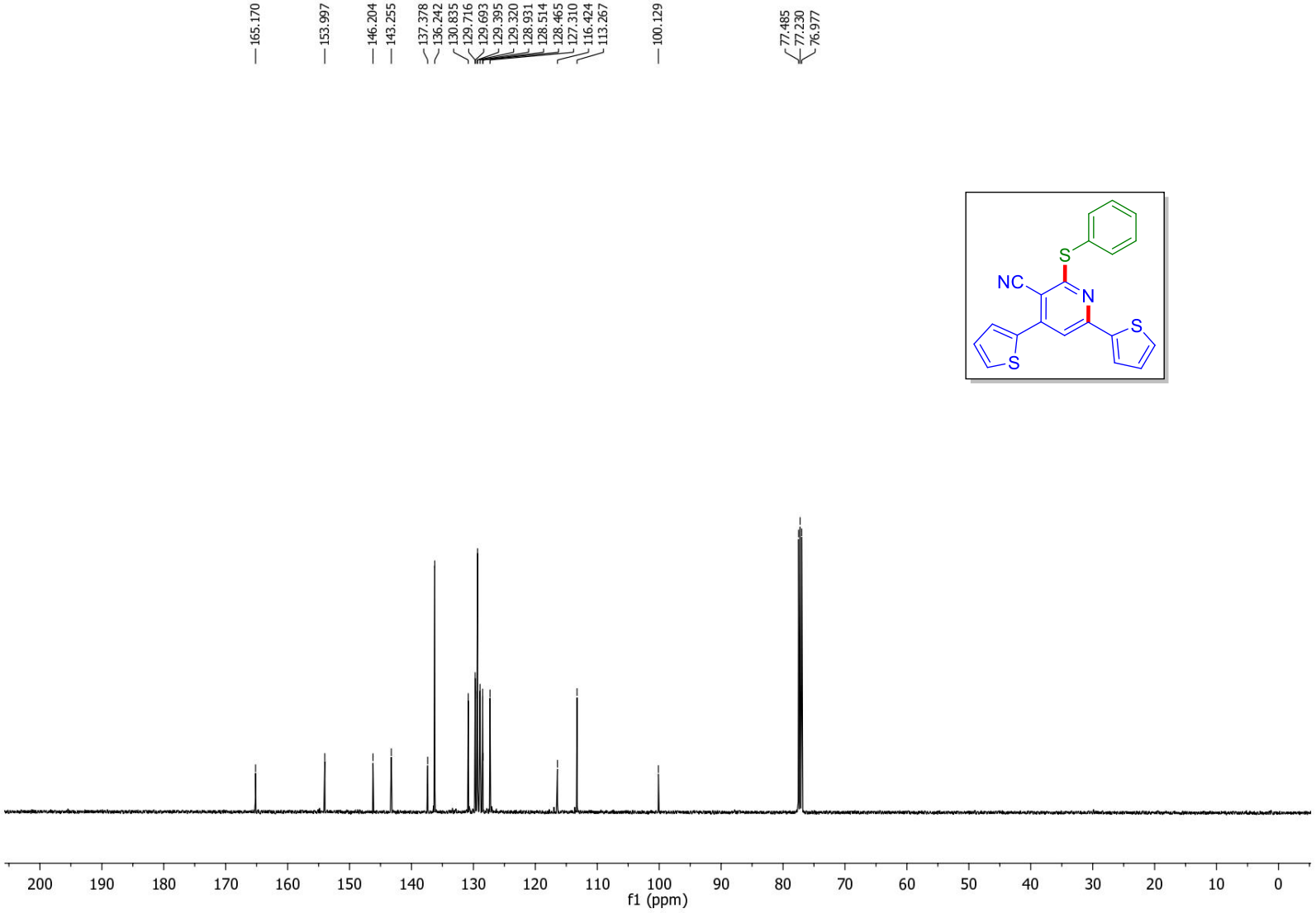


2-(Phenylthio)-4,6-di(thiophen-2-yl)nicotinonitrile (18a): ^{1}H NMR ($CDCl_3$, 500 MHz)

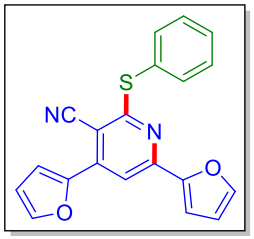


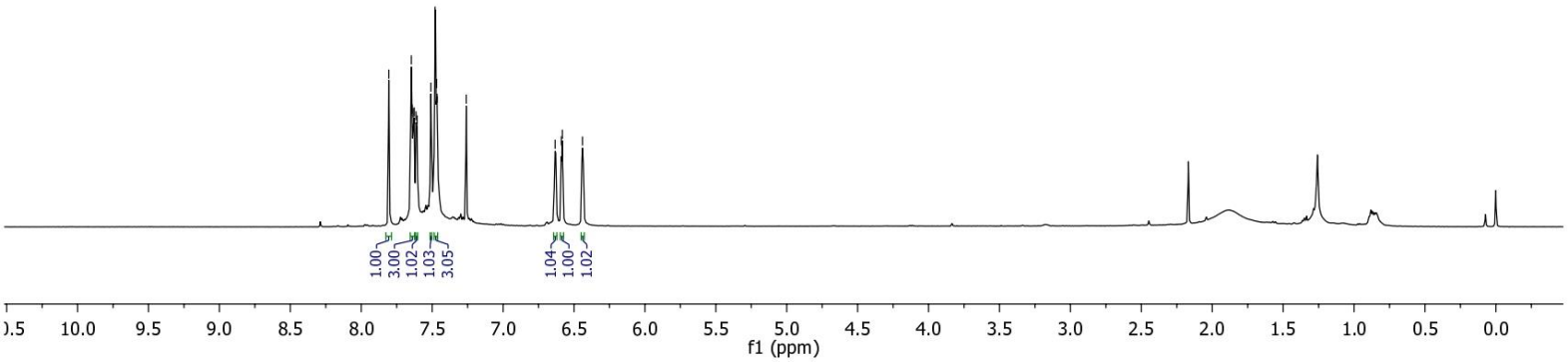


2-(Phenylthio)-4,6-di(thiophen-2-yl)nicotinonitrile (18a): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)

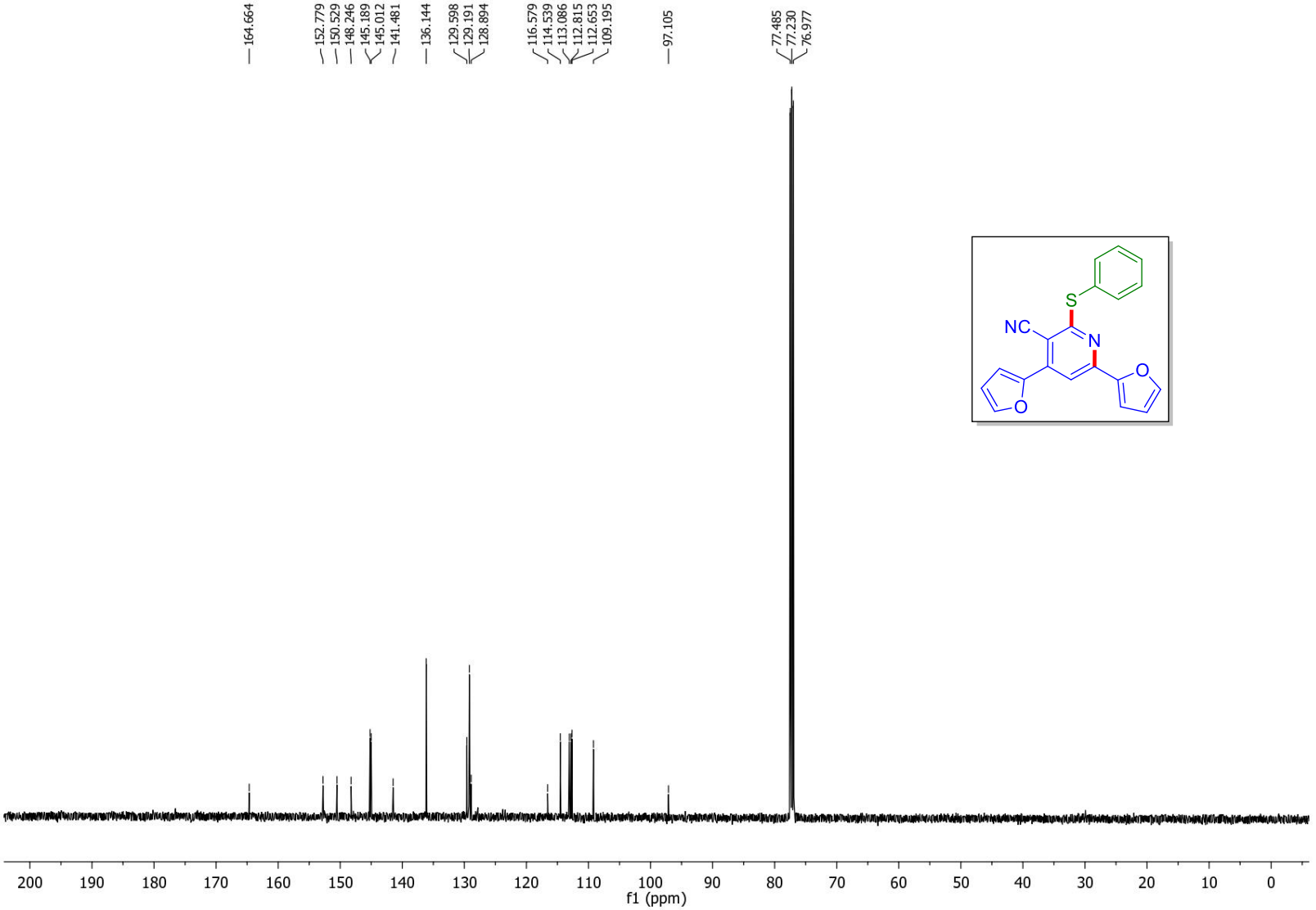


4,6-Di(furan-2-yl)-2-(phenylthio)nicotinonitrile (19a): ^{1}H NMR ($CDCl_3$, 500 MHz)

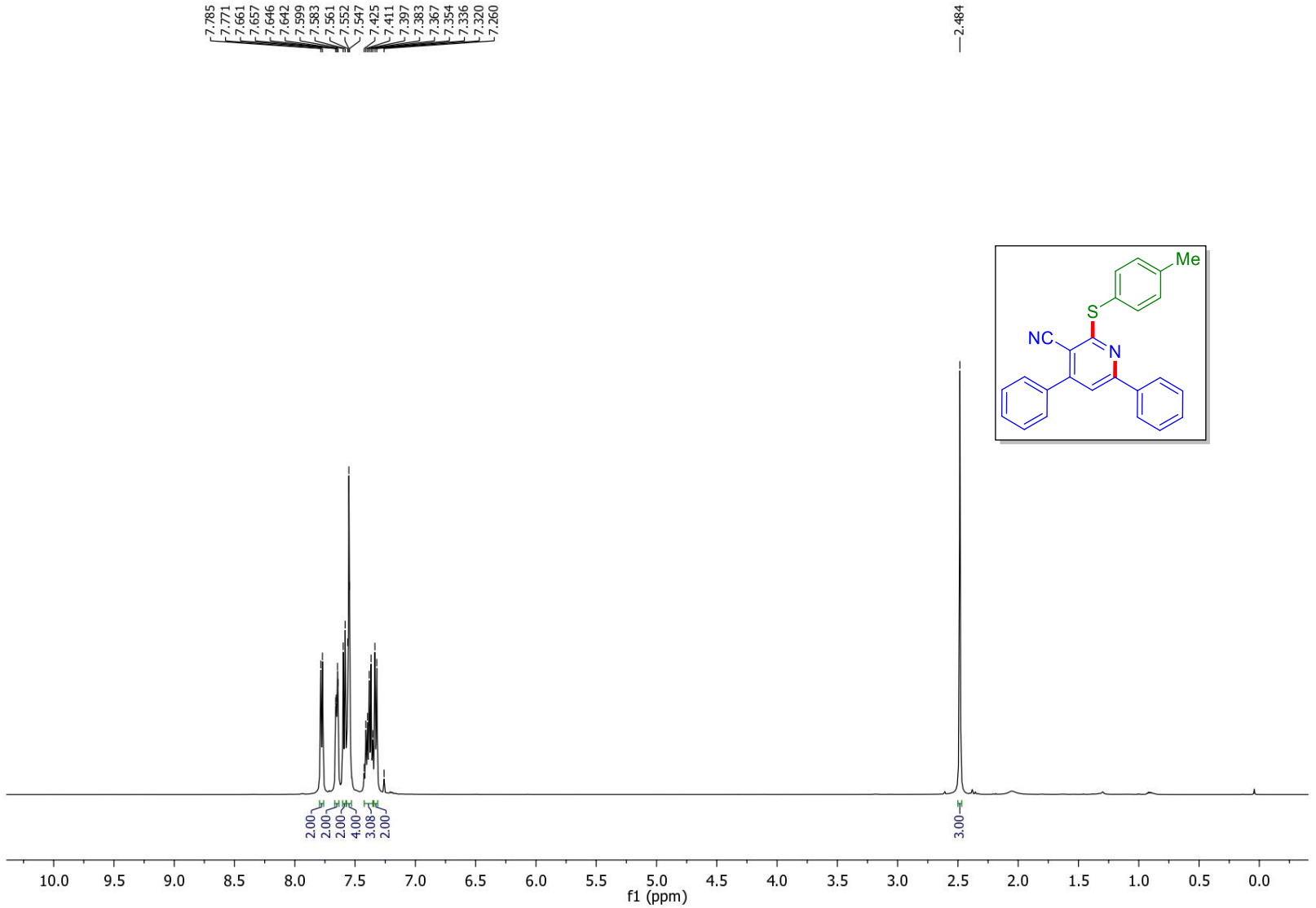




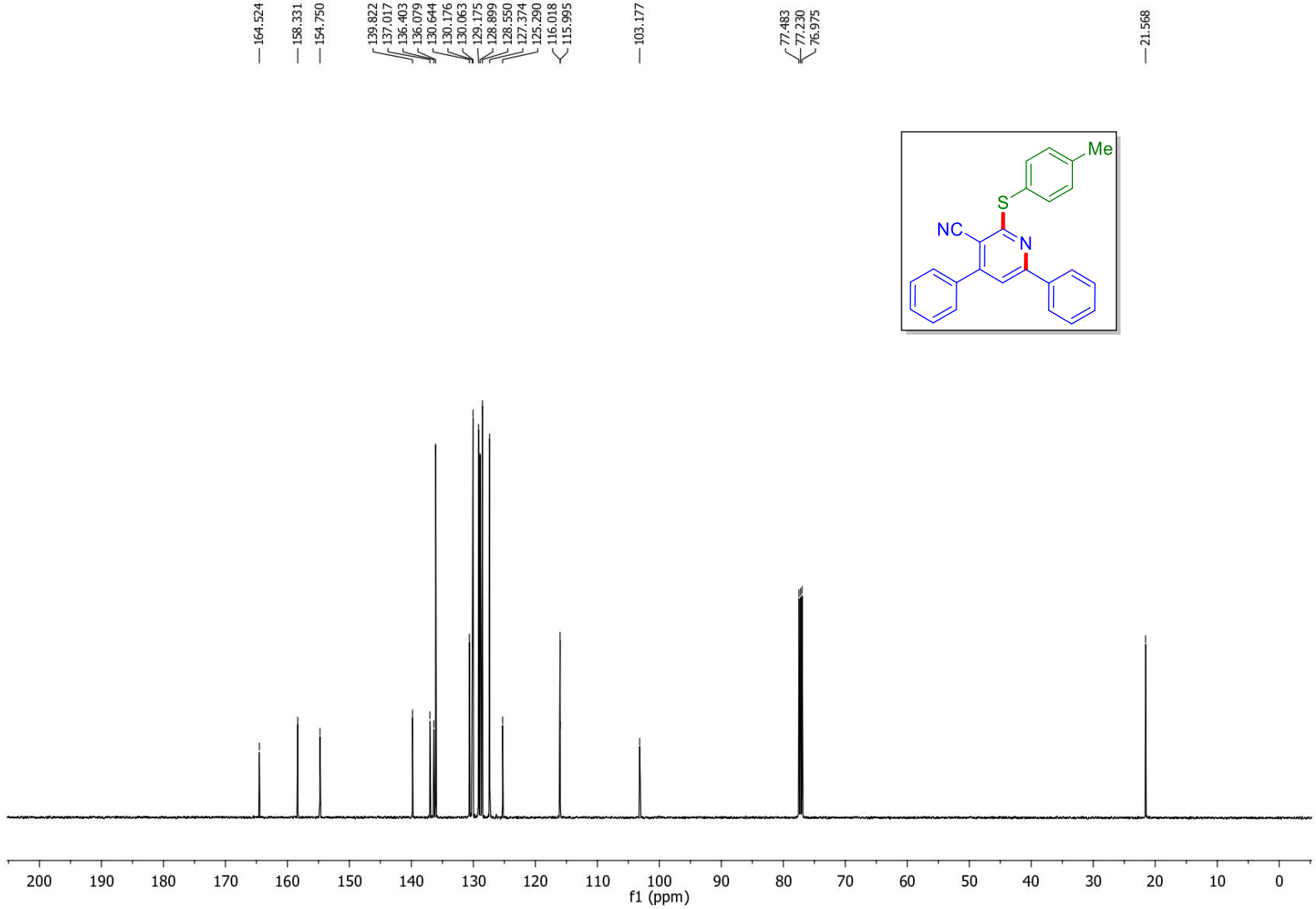
4,6-Di(furan-2-yl)-2-(phenylthio)nicotinonitrile (19a): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



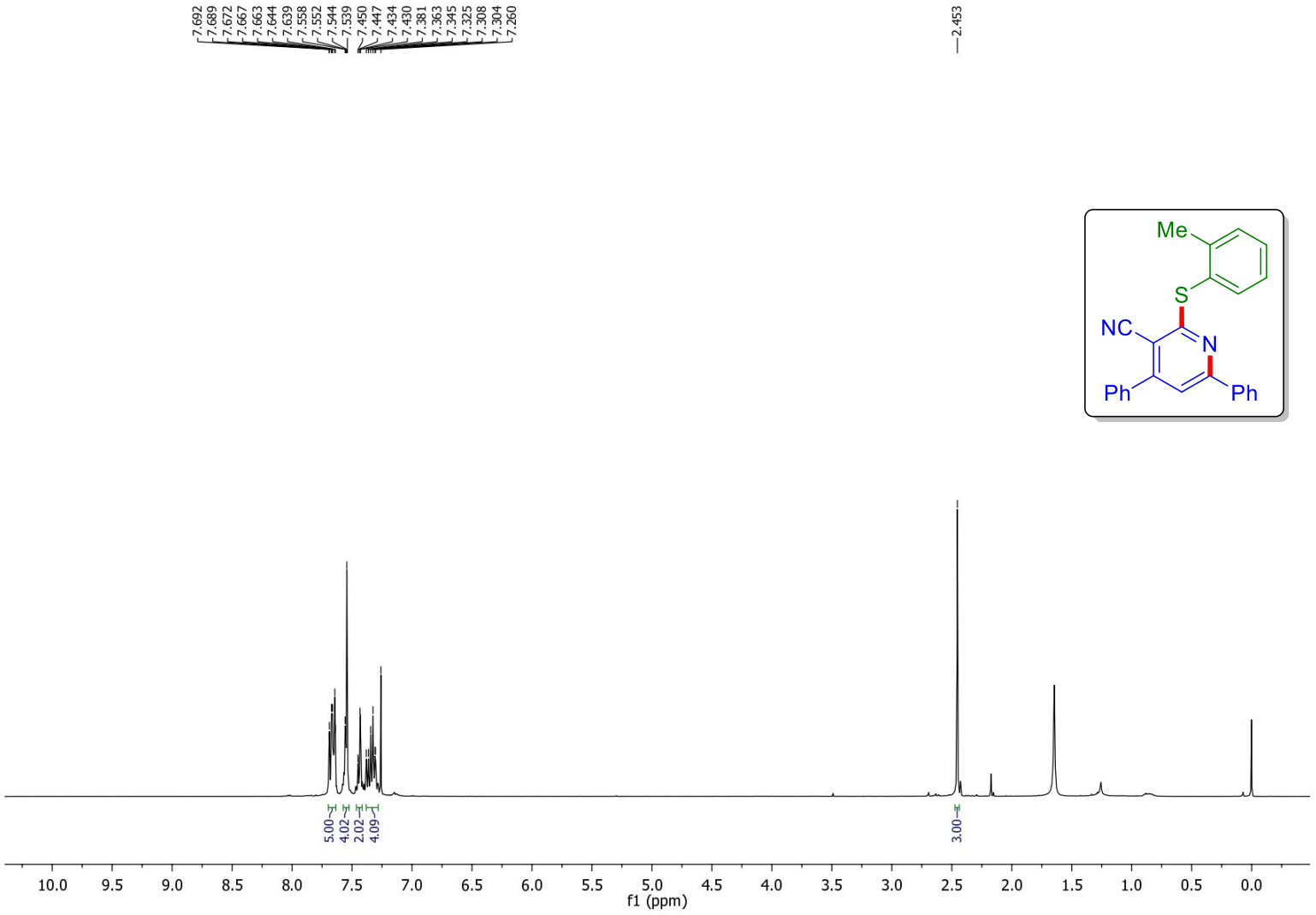
4,6-Diphenyl-2-(p-tolylthio)nicotinonitrile (1b): ^{1}H NMR ($CDCl_3$, 500 MHz)



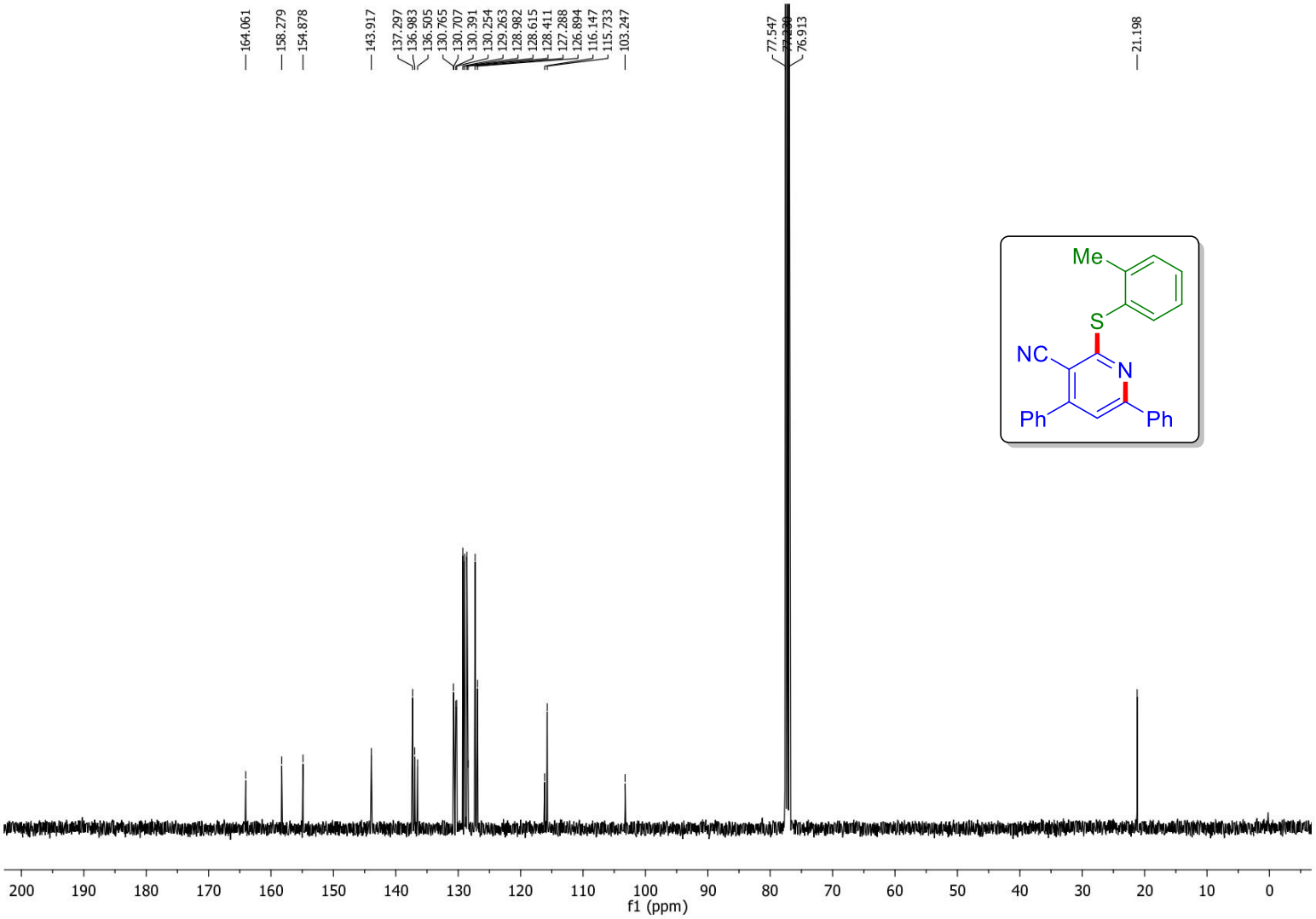
4,6-Diphenyl-2-(p-tolylthio)nicotinonitrile (1b): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



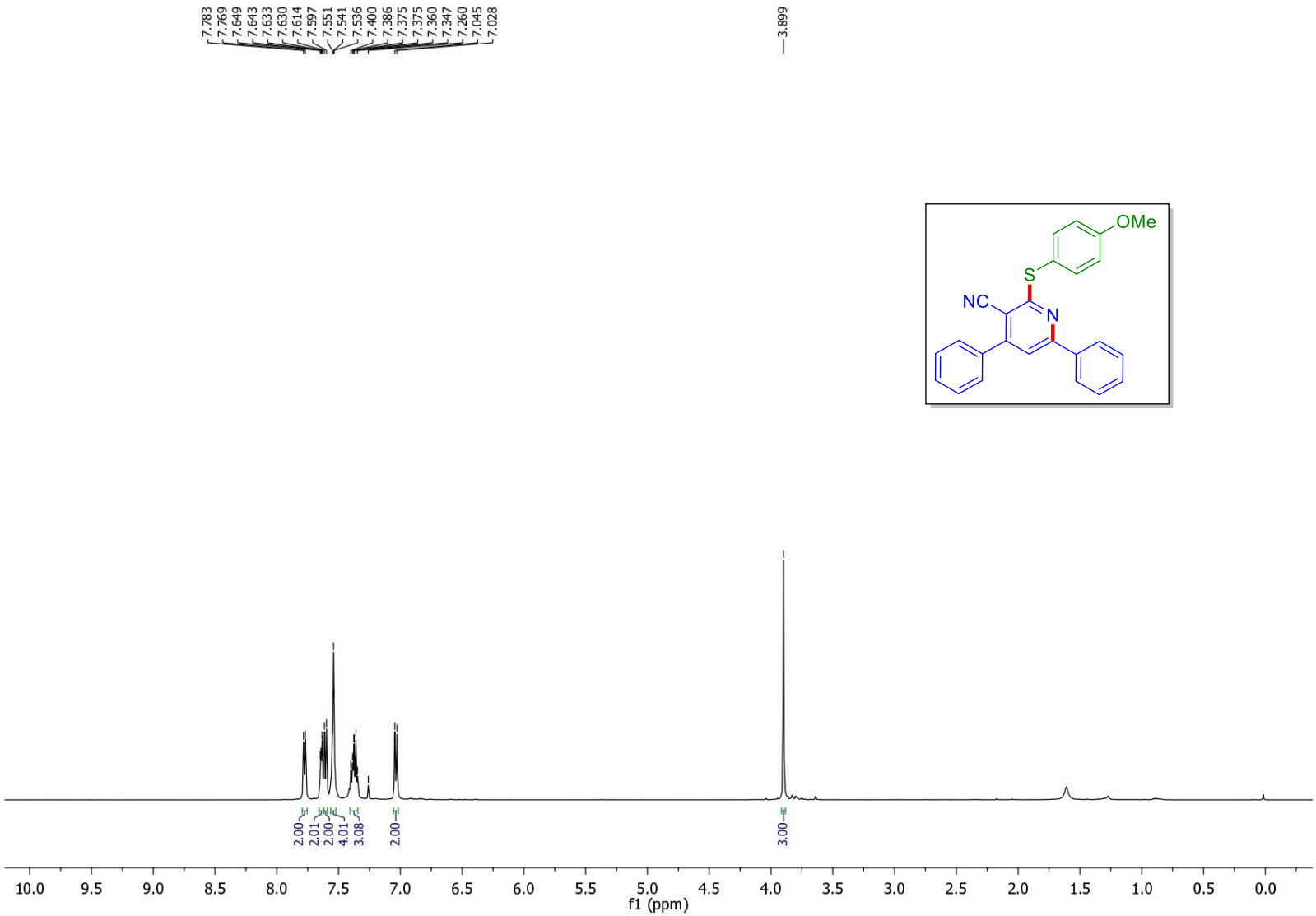
4,6-Diphenyl-2-(o-tolylthio)nicotinonitrile (1c) : ^{1}H NMR ($CDCl_3$, 400 MHz)



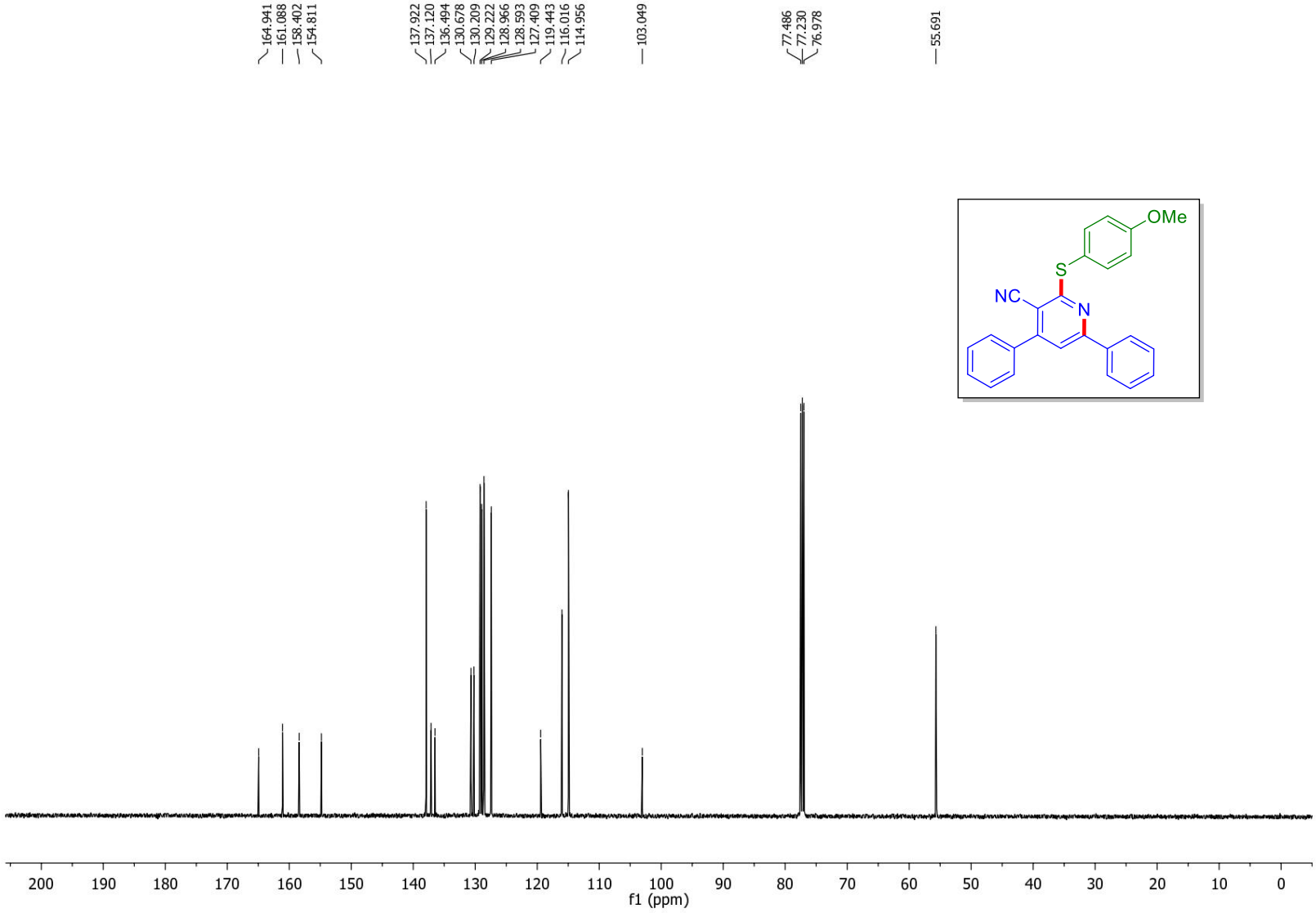
4,6-Diphenyl-2-(o-tolylthio)nicotinonitrile (1c) :$^{13}C\ \{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)



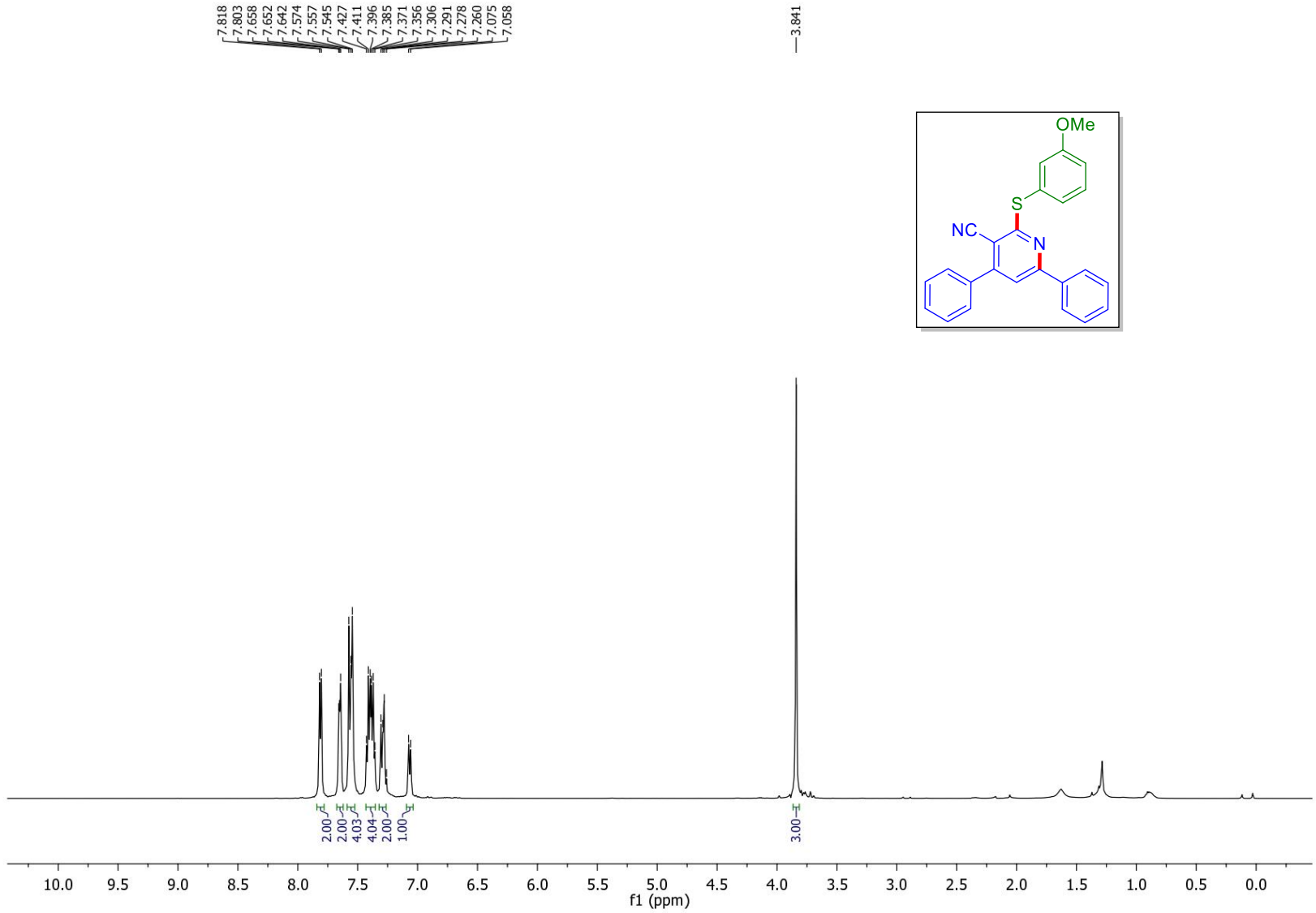
2-((4-Methoxyphenyl)thio)-4,6-diphenylnicotinonitrile (1d): ^{1}H NMR ($CDCl_3$, 500 MHz)



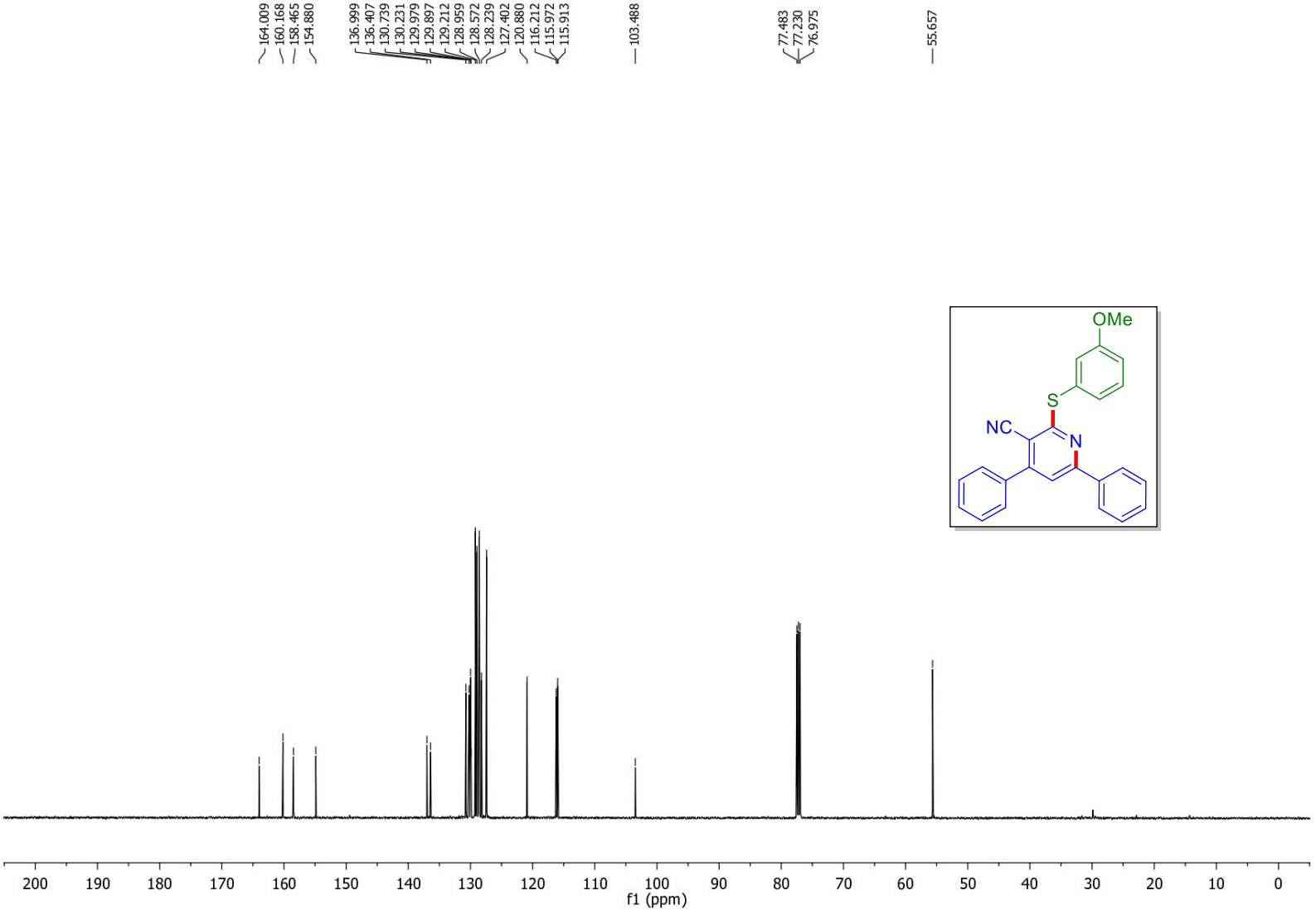
2-((4-Methoxyphenyl)thio)-4,6-diphenylnicotinonitrile (1d): ^{13}C {^{1}H} NMR ($CDCl_3$, 125 MHz)



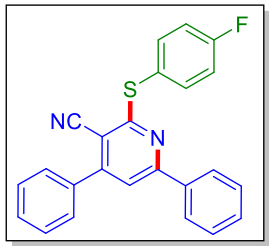
2-((3-Methoxyphenyl)thio)-4,6-diphenylnicotinonitrile (1e): ^{1}H NMR ($CDCl_3$, 500 MHz)

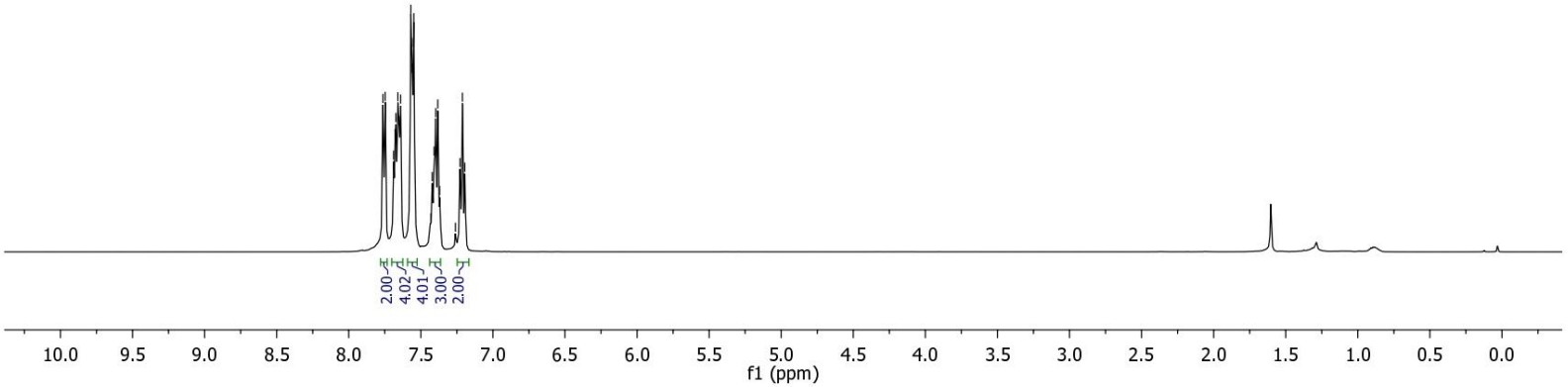


2-((3-Methoxyphenyl)thio)-4,6-diphenylnicotinonitrile (1e): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)

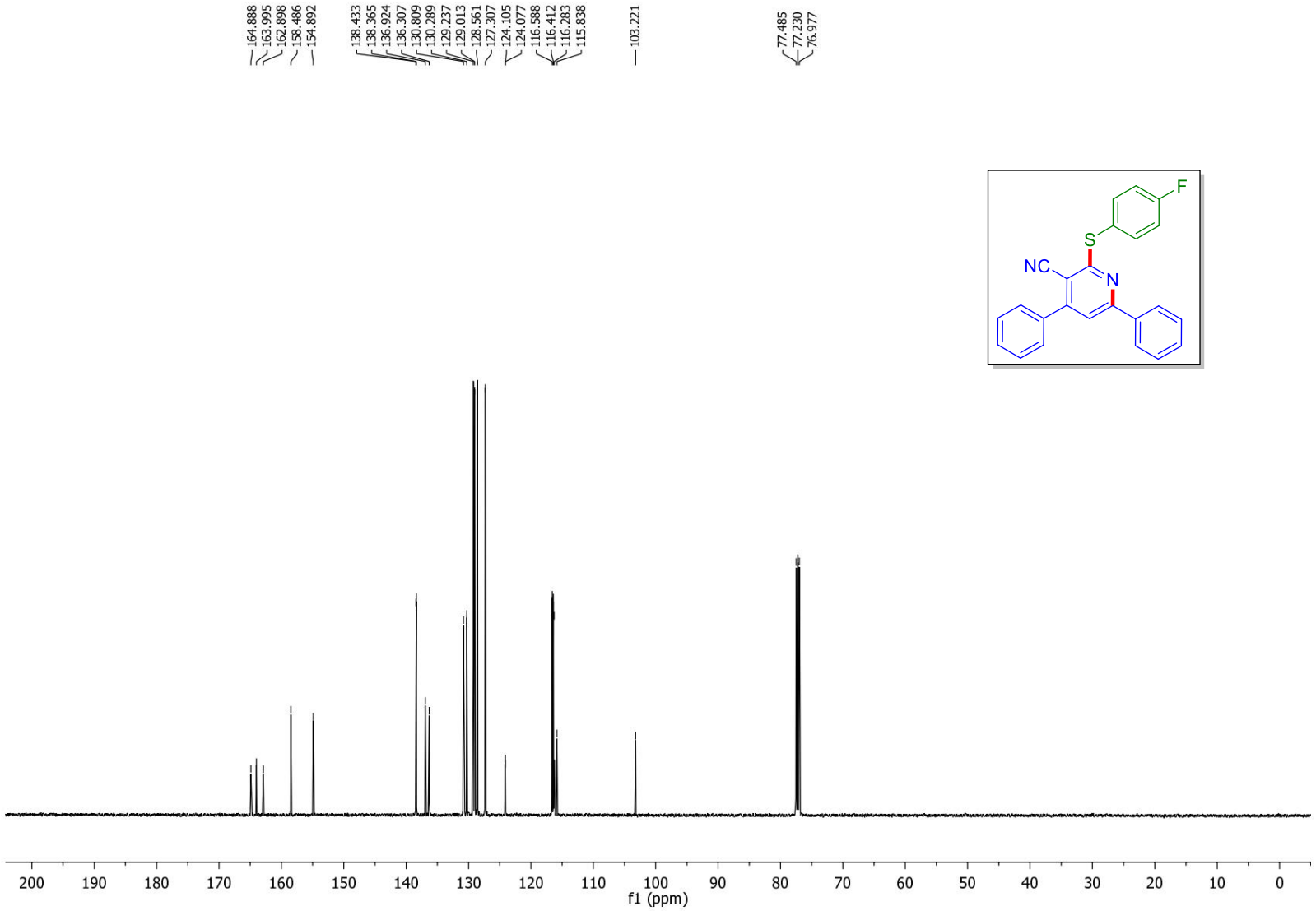


2-((4-Fluorophenyl)thio)-4,6-diphenylnicotinonitrile (1f): ^{1}H NMR ($CDCl_3$, 500 MHz)

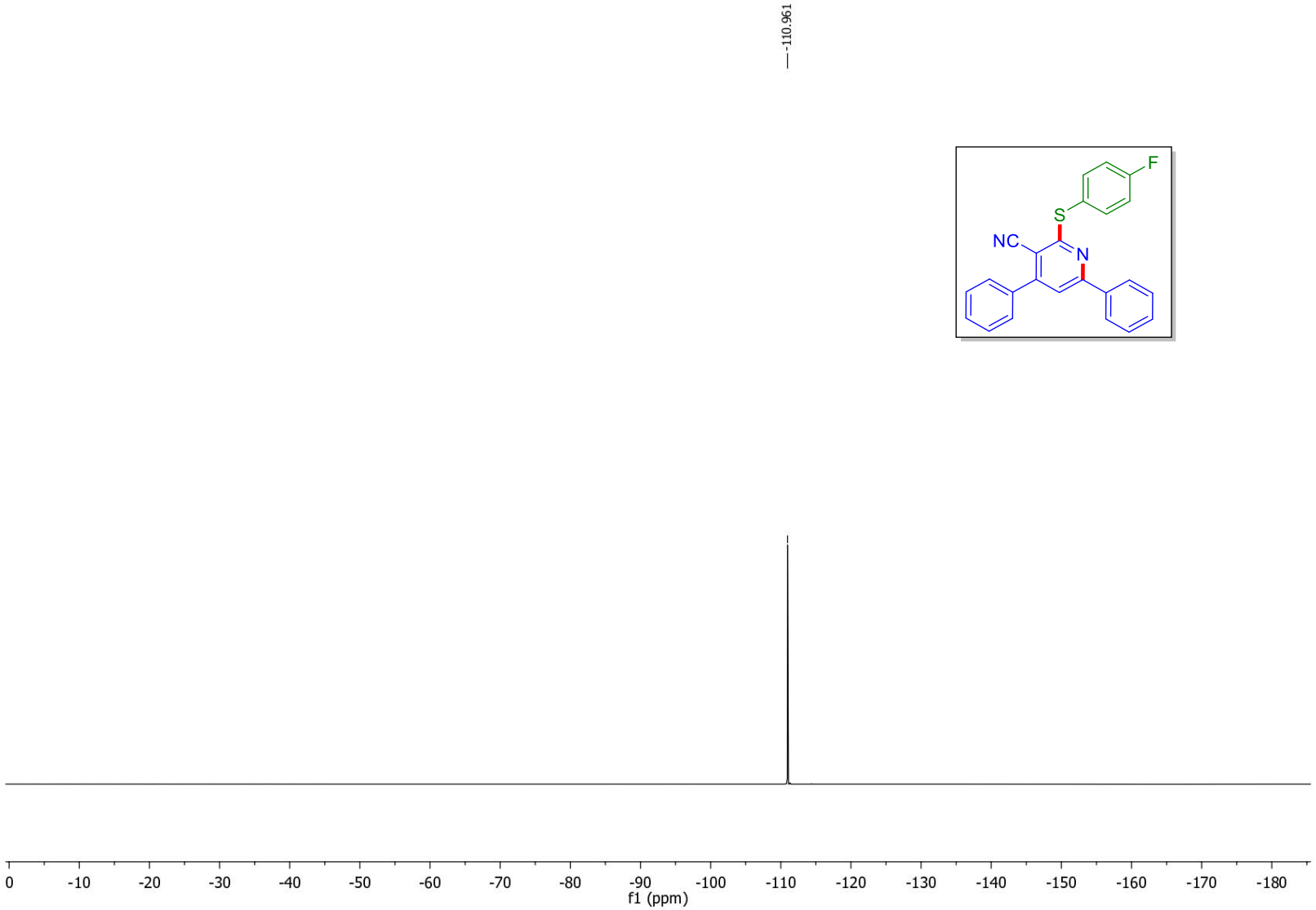




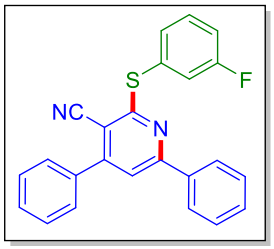
2-((4-Fluorophenyl)thio)-4,6-diphenylnicotinonitrile (1f): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)

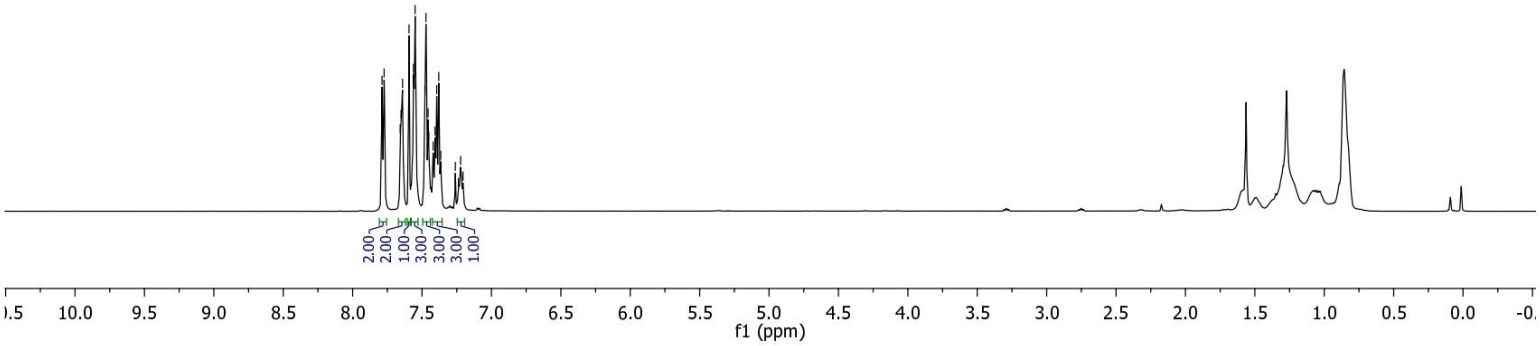


2-((4-Fluorophenyl)thio)-4,6-diphenylnicotinonitrile (1f) : ^{19}F NMR ($CDCl_3$, 471 MHz)

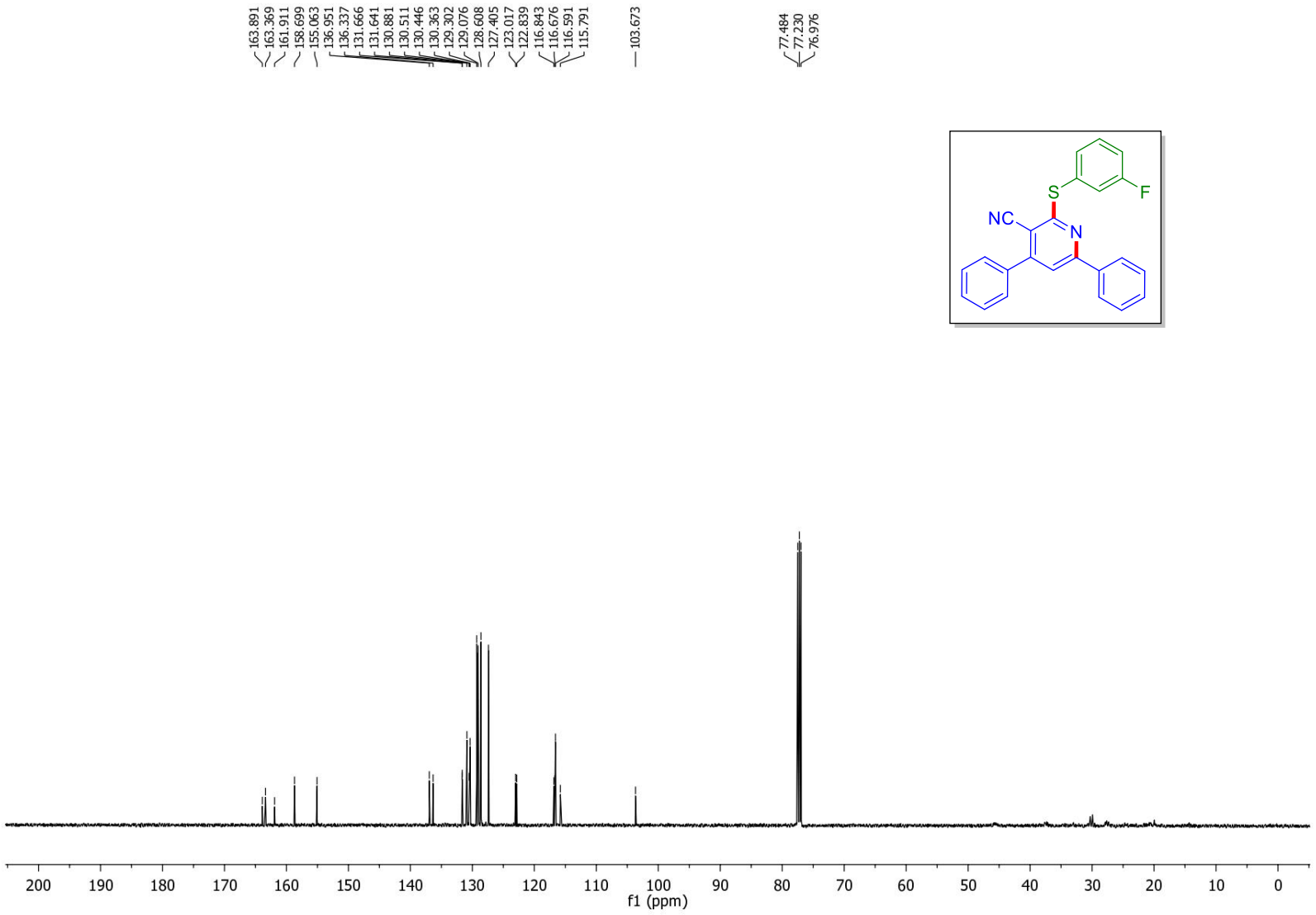


2-((3-Fluorophenyl)thio)-4,6-diphenylnicotinonitrile (1g): ^{1}H NMR (CDCl$_3$, 500 MHz)

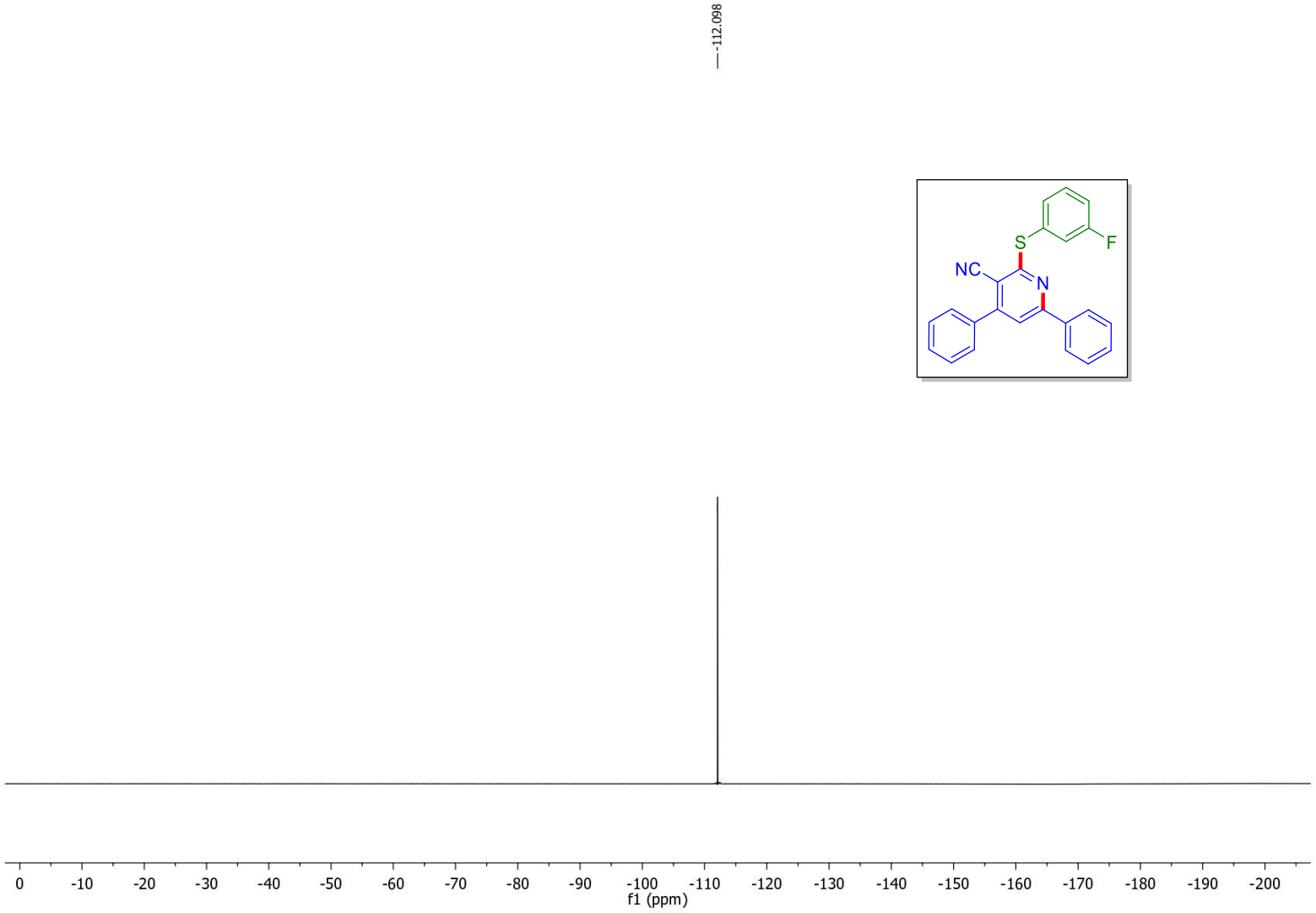




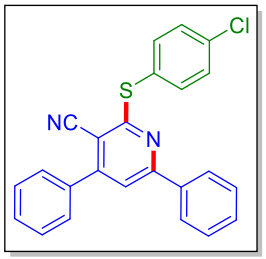
2-((3-Fluorophenyl)thio)-4,6-diphenylnicotinonitrile (1g): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)

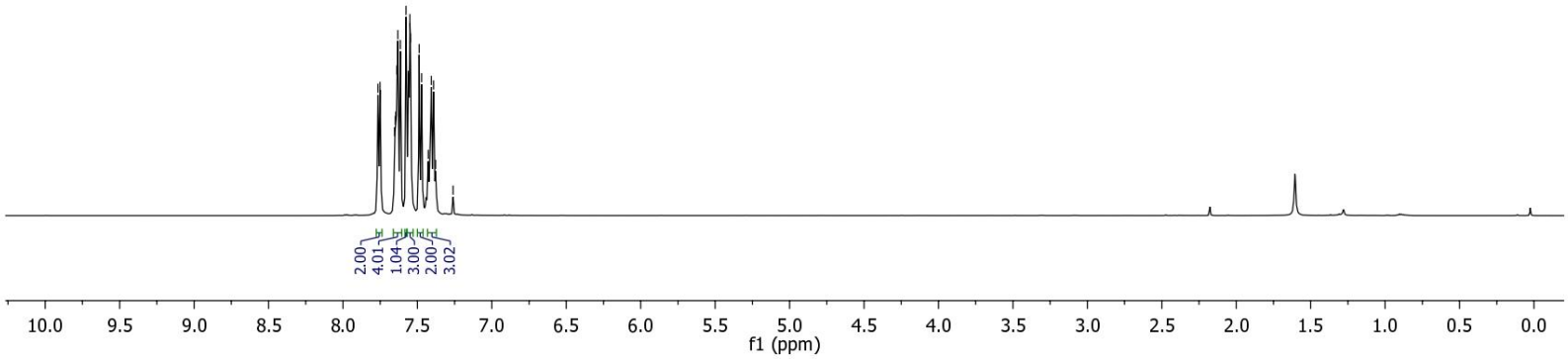


2-((3-Fluorophenyl)thio)-4,6-diphenylnicotinonitrile (1g): ^{19}F NMR ($CDCl_3$, 471 MHz)

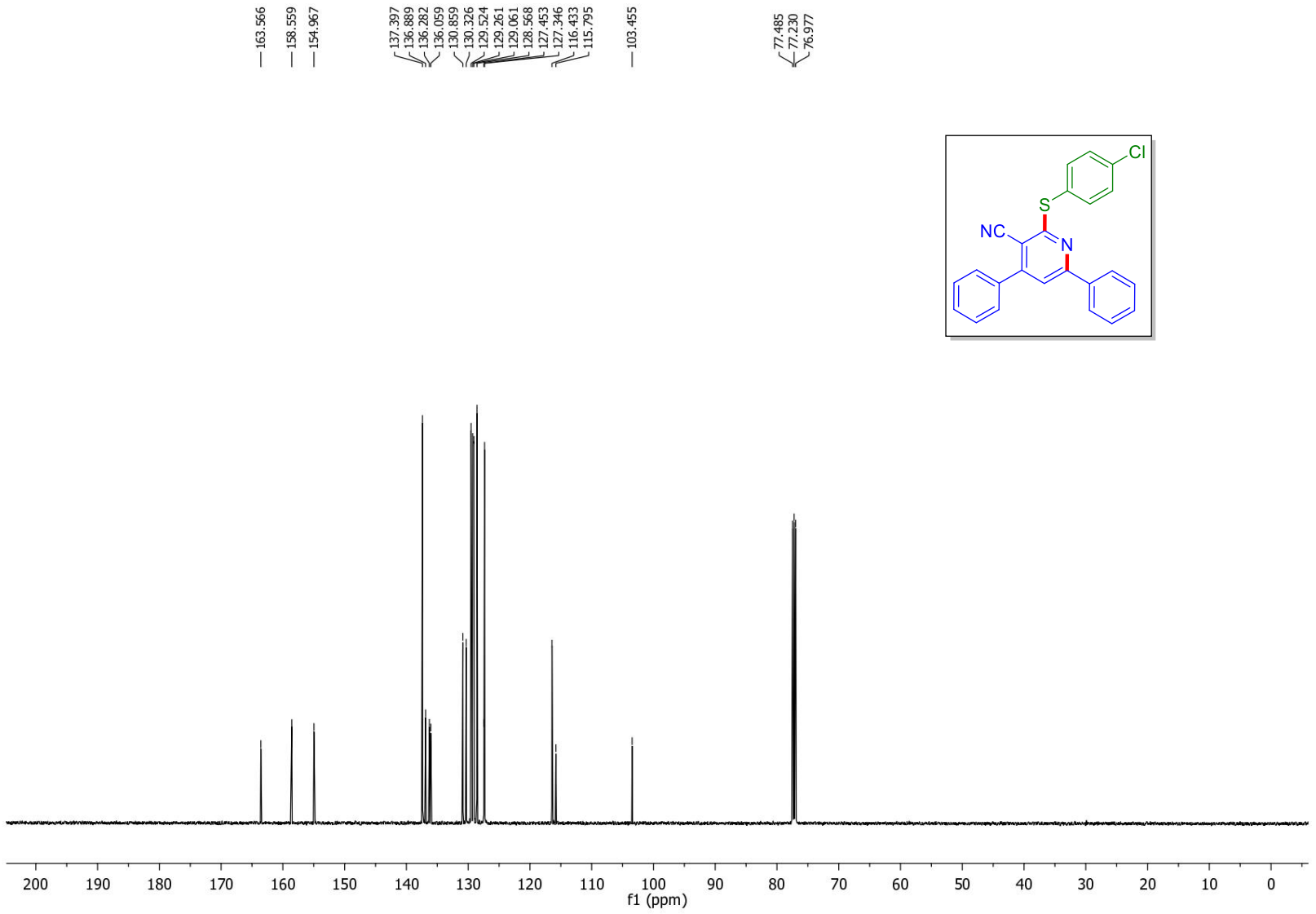


2-((4-Chlorophenyl)thio)-4,6-diphenylnicotinonitrile (1h): ^{1}H NMR ($CDCl_3$, 500 MHz)

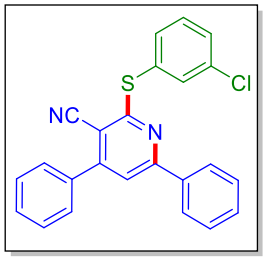


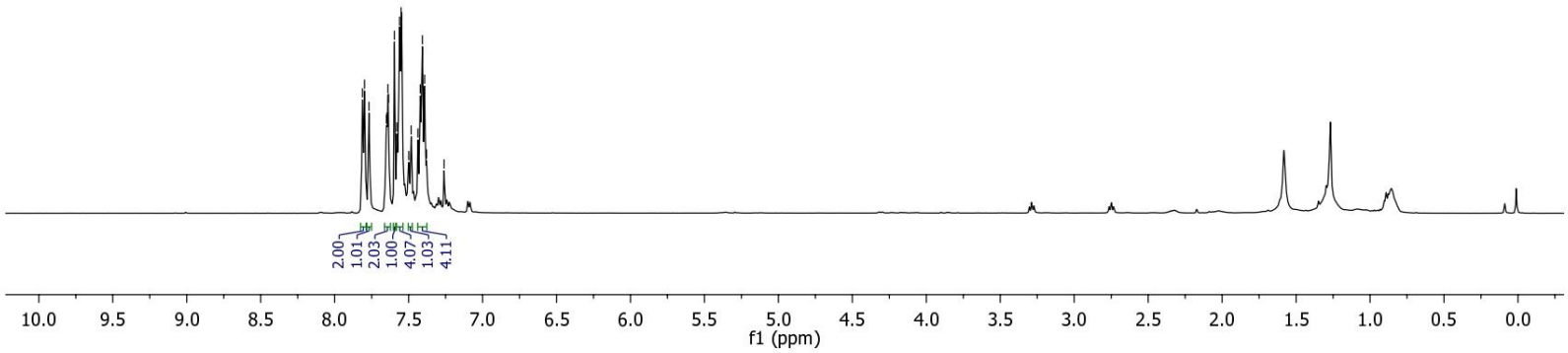


2-((4-Chlorophenyl)thio)-4,6-diphenylnicotinonitrile (1h): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)

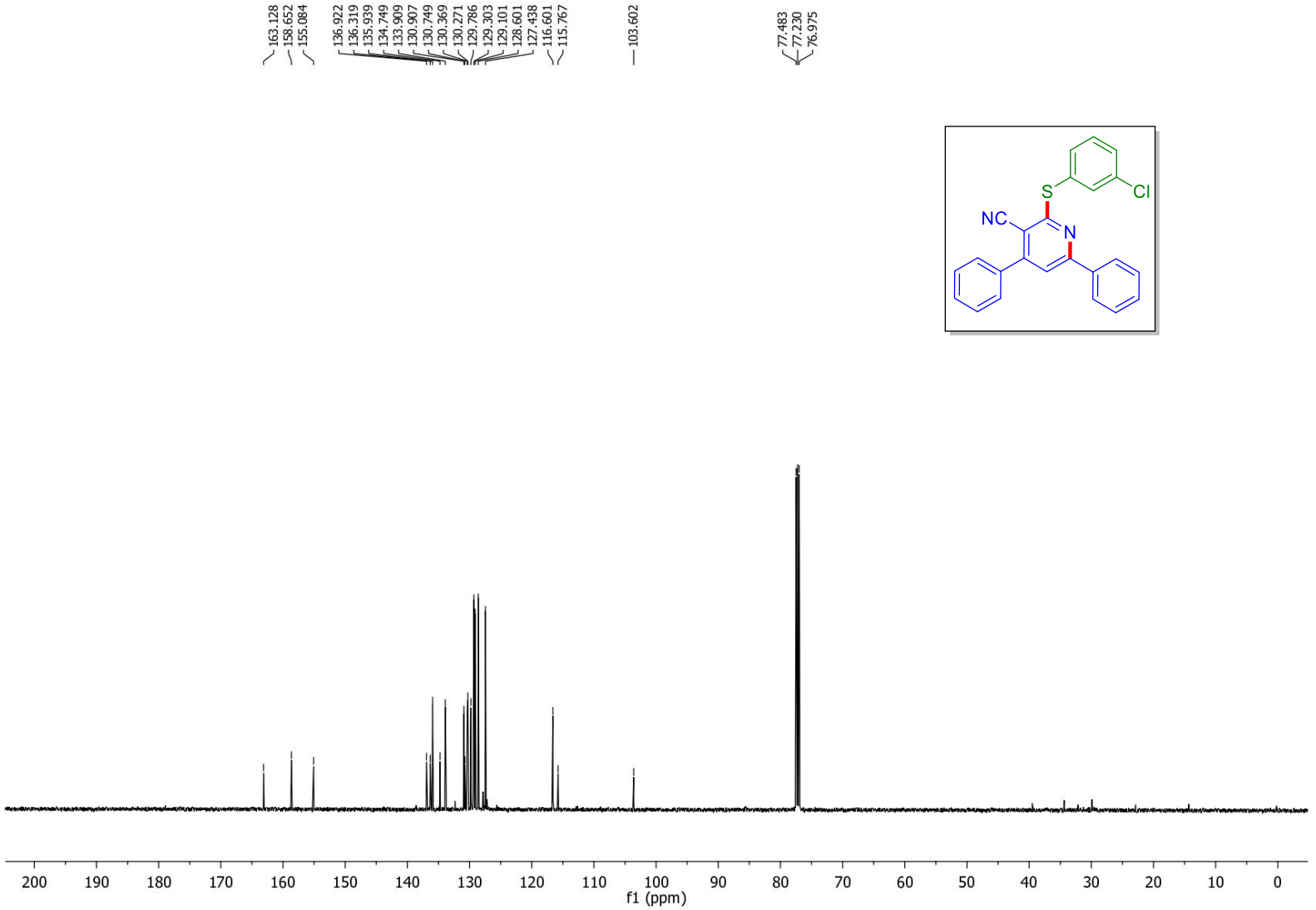


2-((3-Chlorophenyl)thio)-4,6-diphenylnicotinonitrile (1i): ^{1}H NMR ($CDCl_3$, 500 MHz)

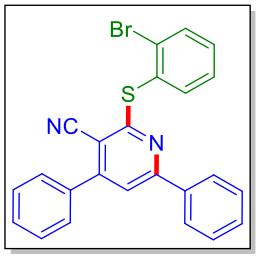


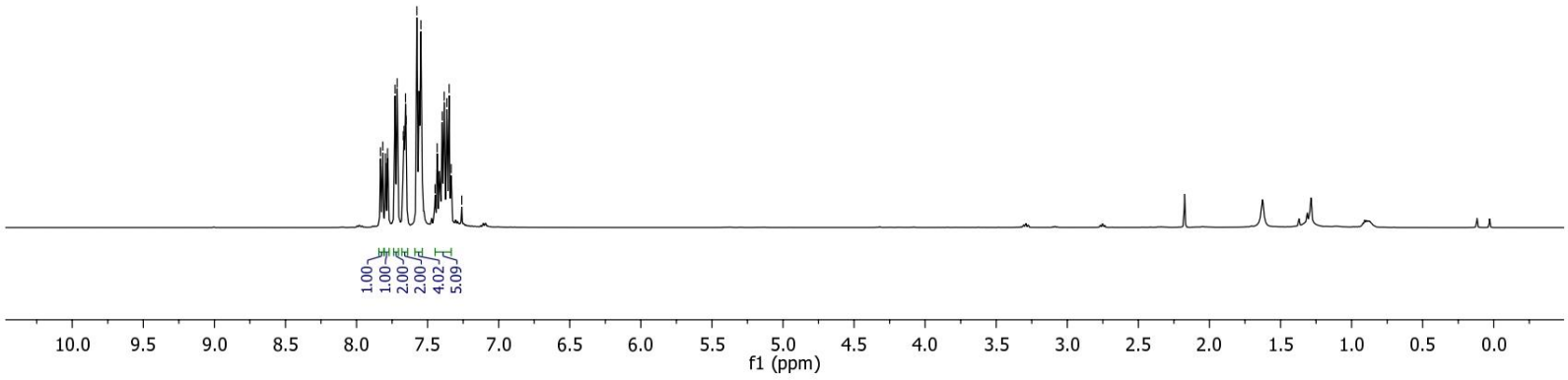


2-((3-Chlorophenyl)thio)-4,6-diphenylnicotinonitrile (1i): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)

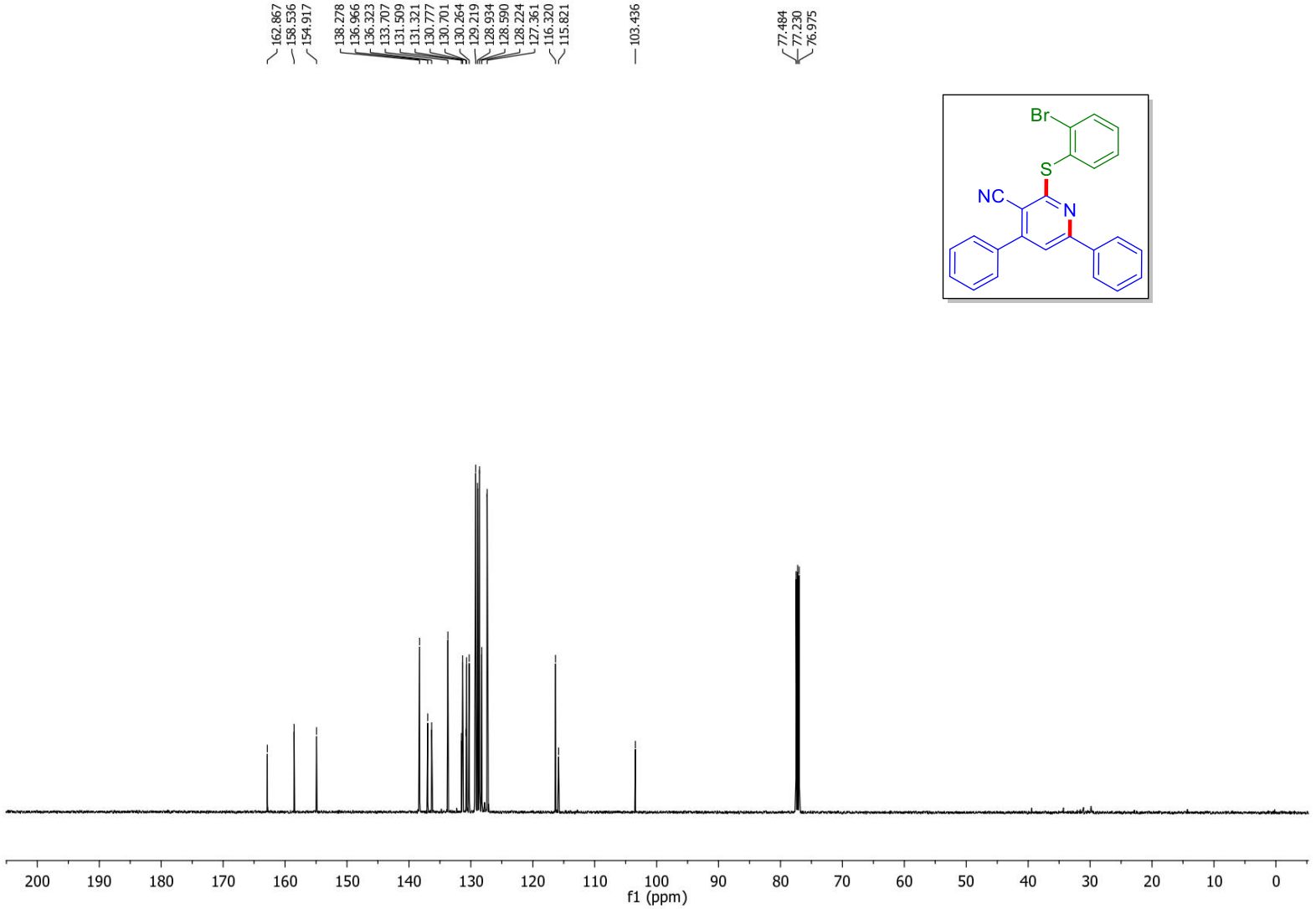


2-((2-Bromophenyl)thio)-4,6-diphenylnicotinonitrile (1j): ^{1}H NMR ($CDCl_3$, 500 MHz)

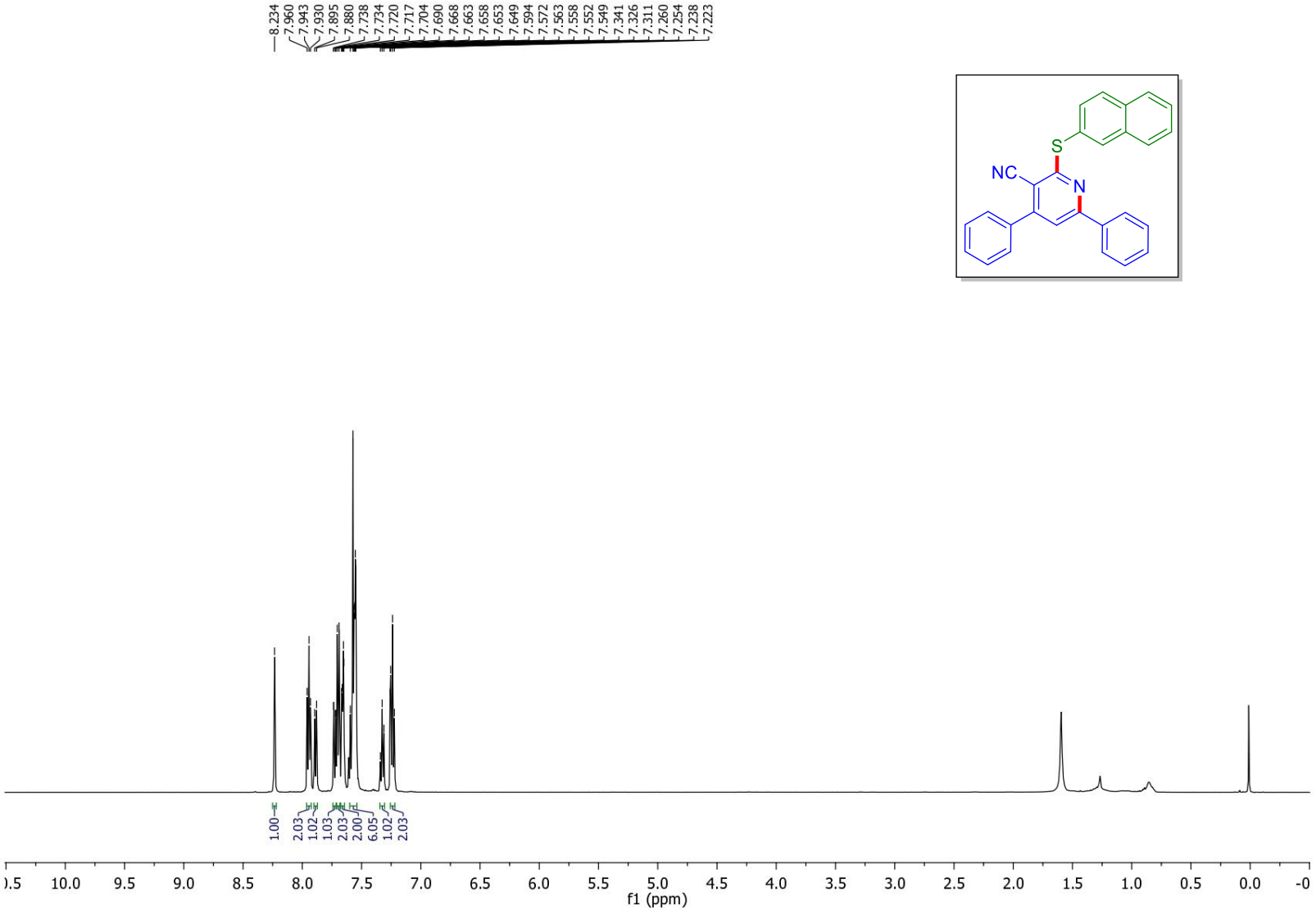




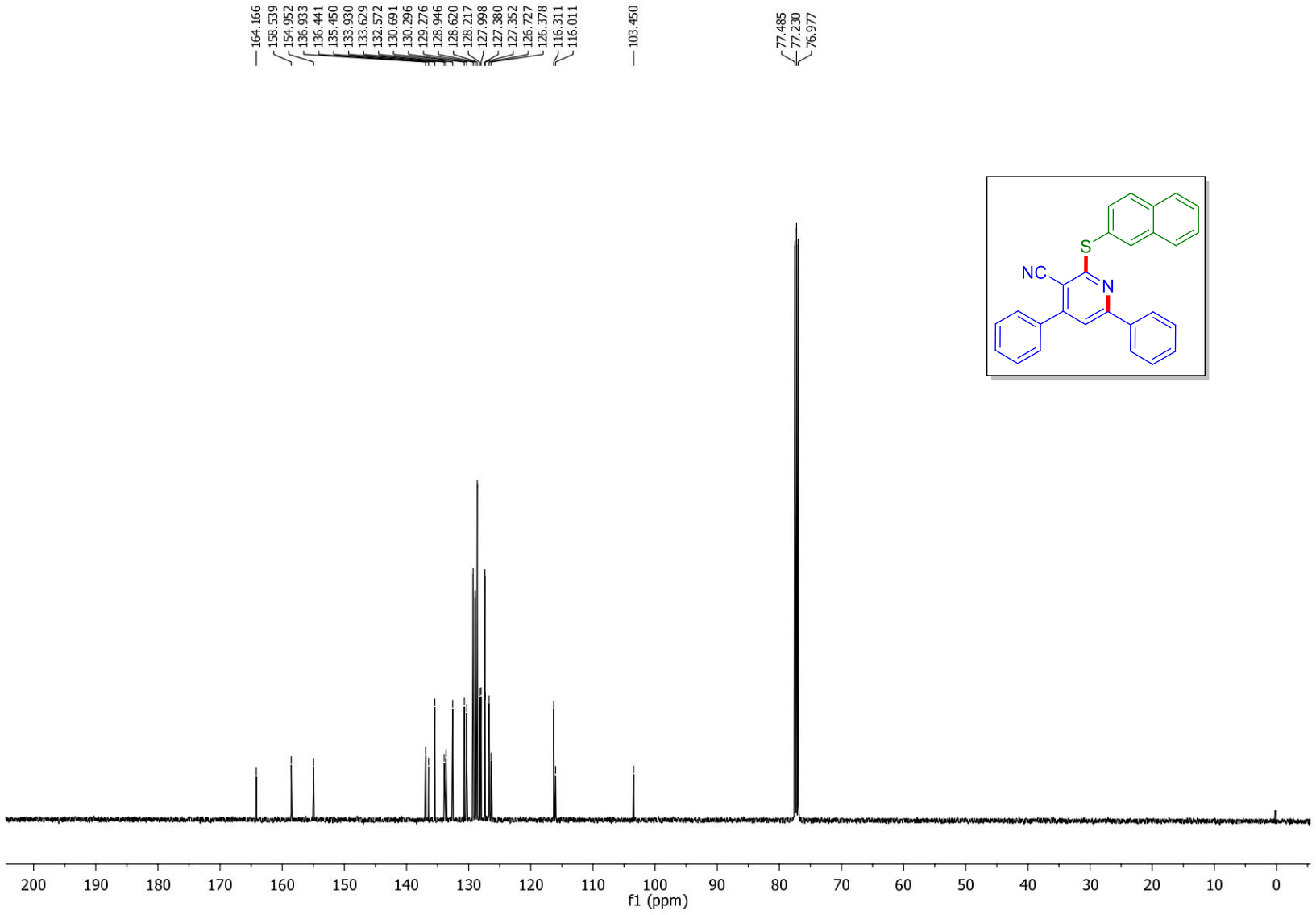
2-((2-Bromophenyl)thio)-4,6-diphenylnicotinonitrile (1j): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



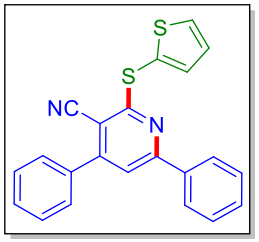
2-(Naphthalen-2-ylthio)-4,6-diphenylnicotinonitrile (1k): ^{1}H NMR ($CDCl_3$, 500 MHz)

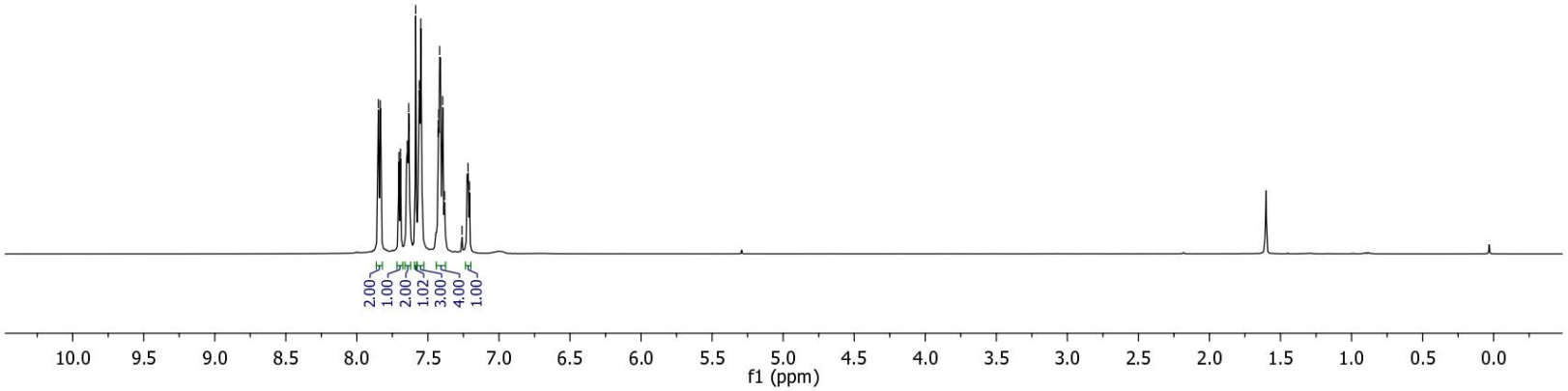


2-(Naphthalen-2-ylthio)-4,6-diphenylnicotinonitrile (1k): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)

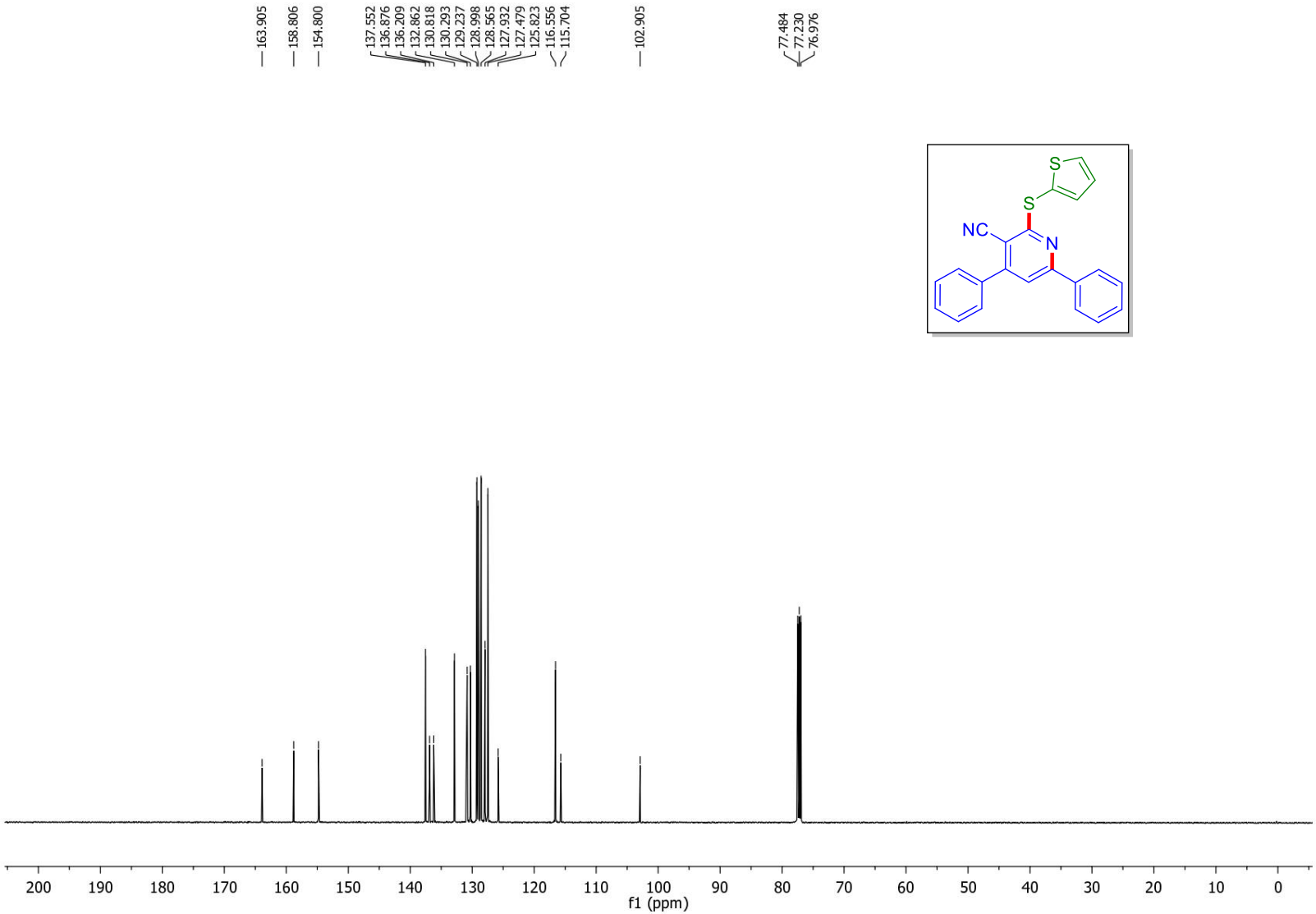


4,6-Diphenyl-2-(thiophen-2-ylthio)nicotinonitrile (1l): ^{1}H NMR (CDCl$_3$, 500 MHz)

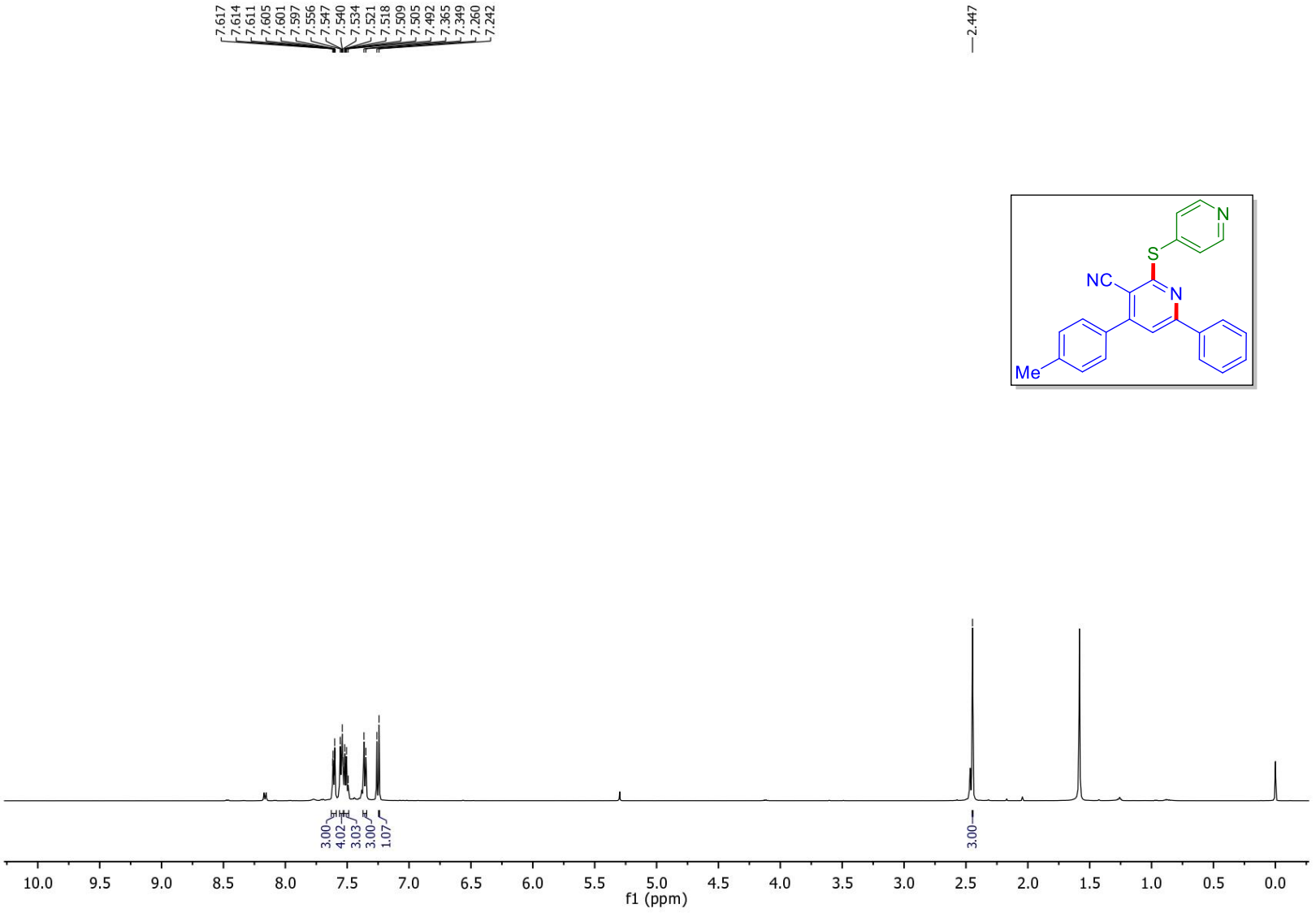




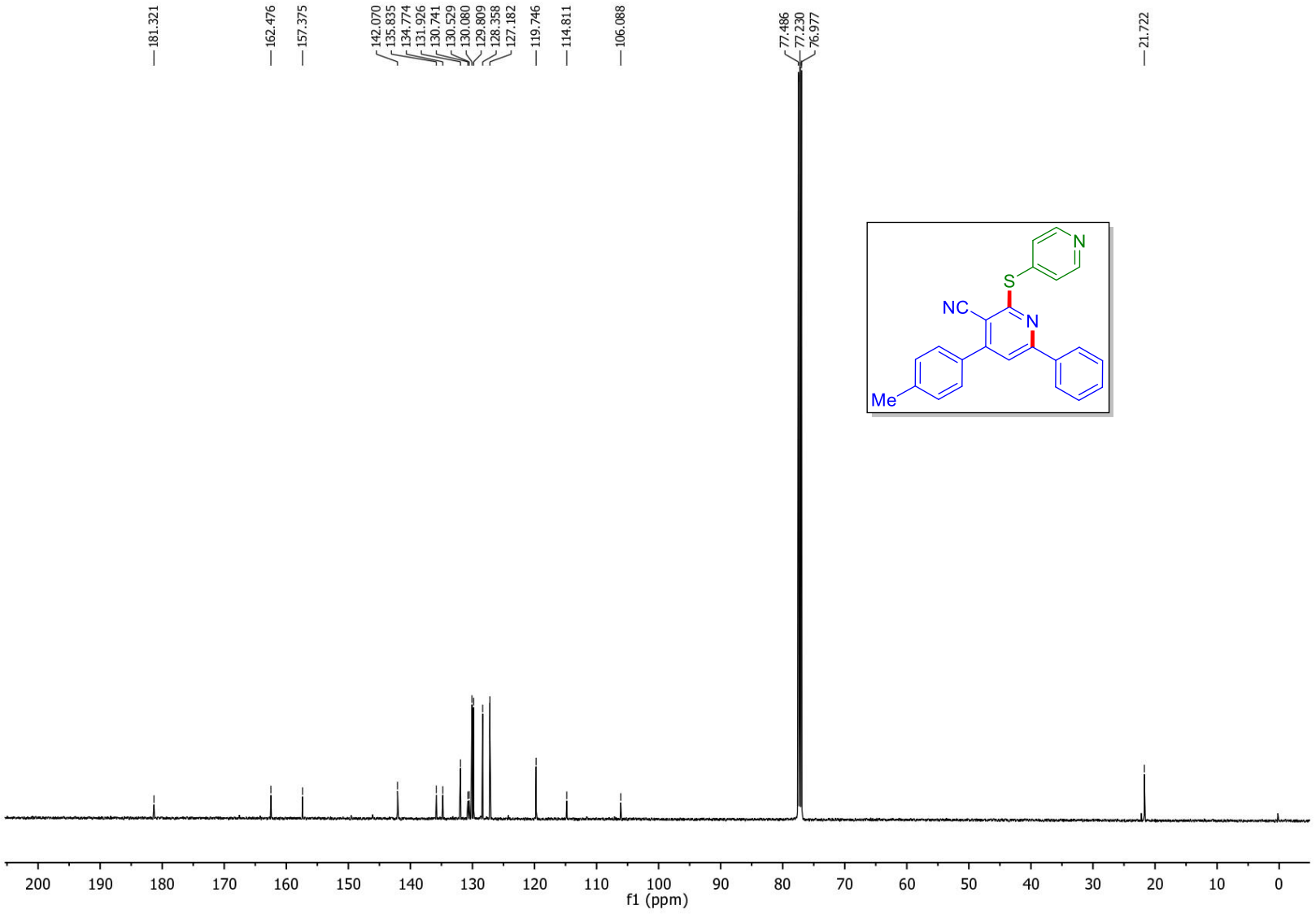
4,6-Diphenyl-2-(thiophen-2-ylthio)nicotinonitrile (1l): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



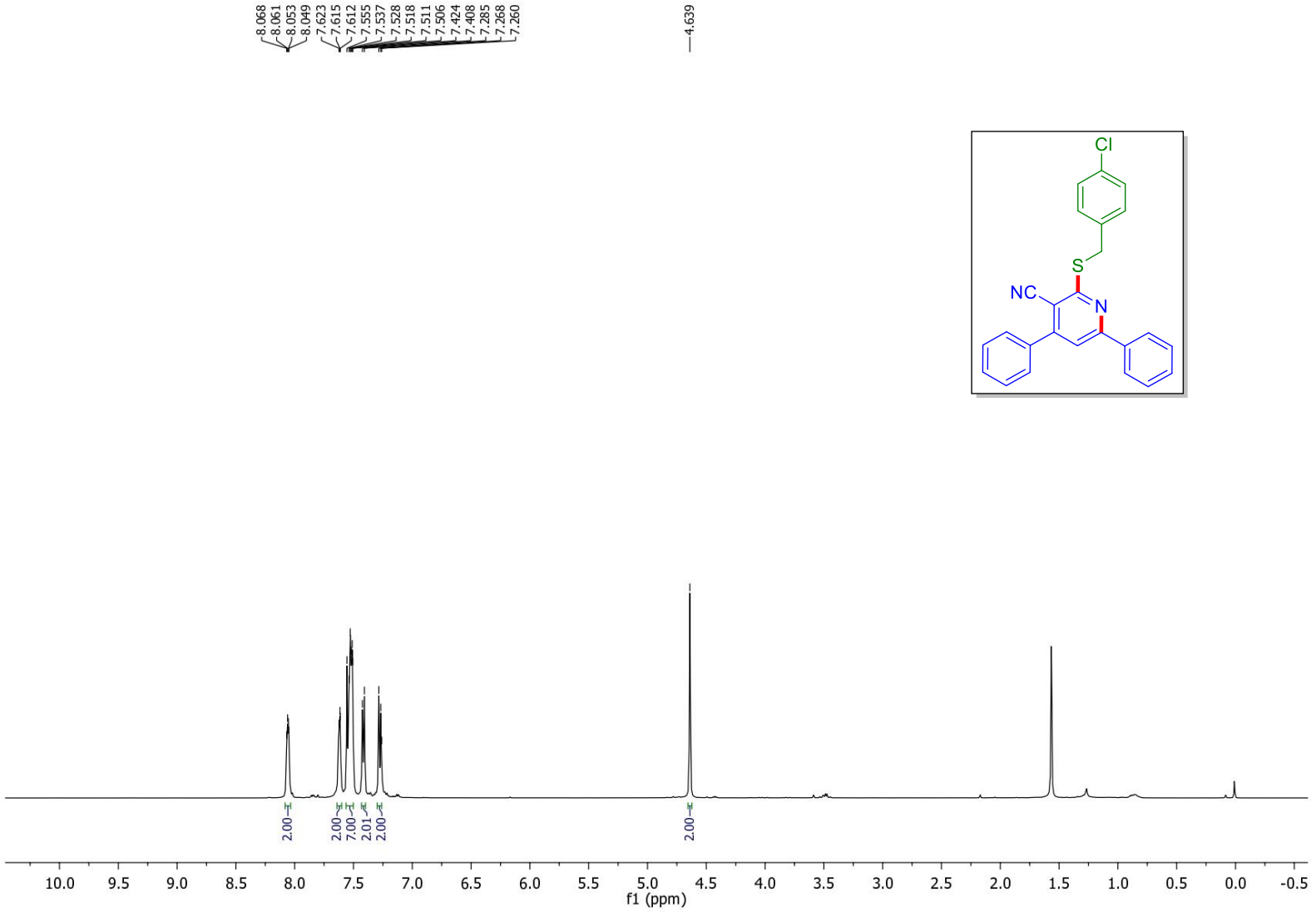
6-Phenyl-2-(pyridin-4-ylthio)-4-(p-tolyl)nicotinonitrile (2m): ^{1}H NMR (CDCl$_3$, 500 MHz)



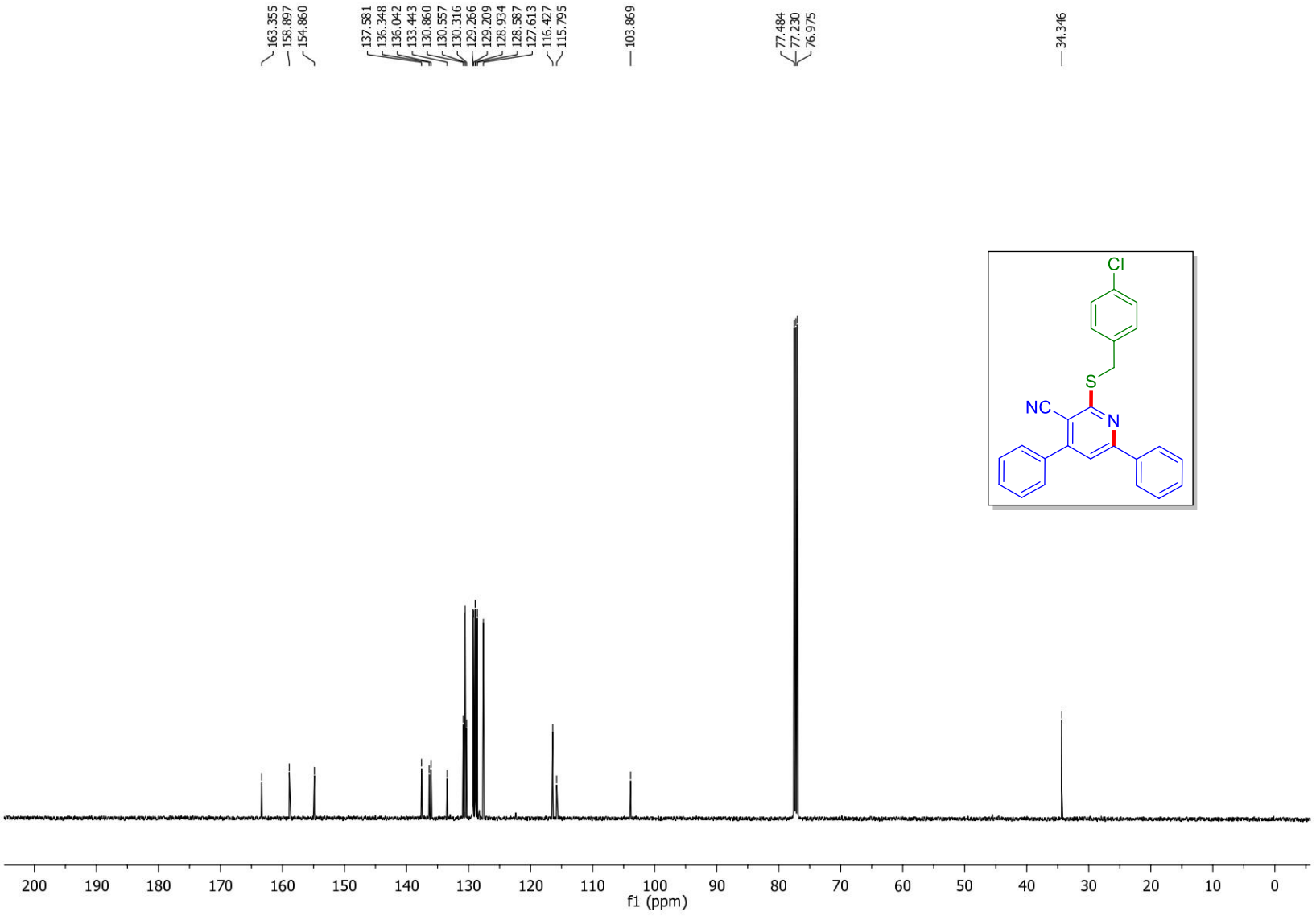
6-Phenyl-2-(pyridin-4-ylthio)-4-(p-tolyl)nicotinonitrile (2m): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



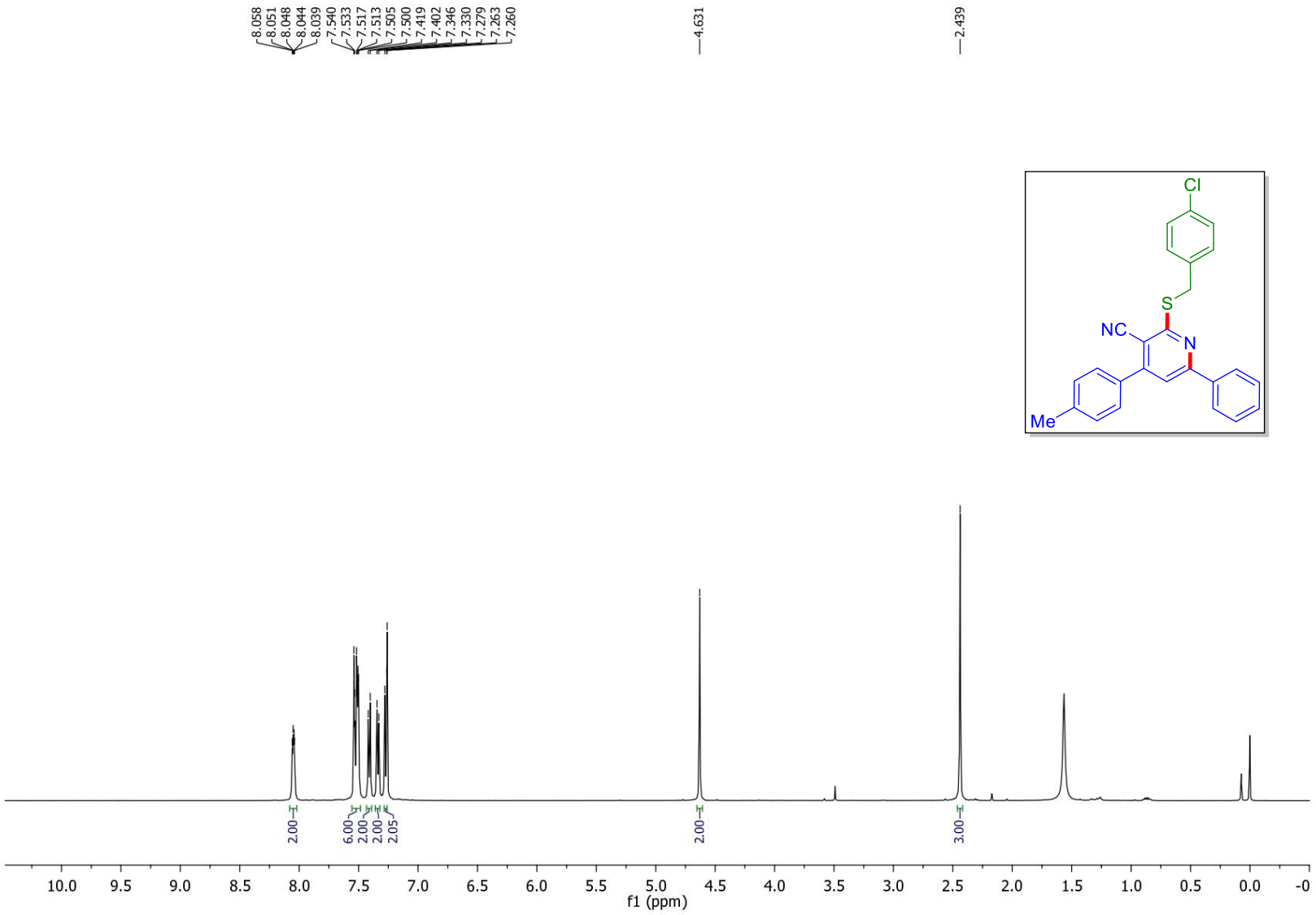
2-((4-Chlorobenzyl)thio)-4,6-diphenylnicotinonitrile (1n): ^{1}H NMR (CDCl$_3$, 500 MHz)



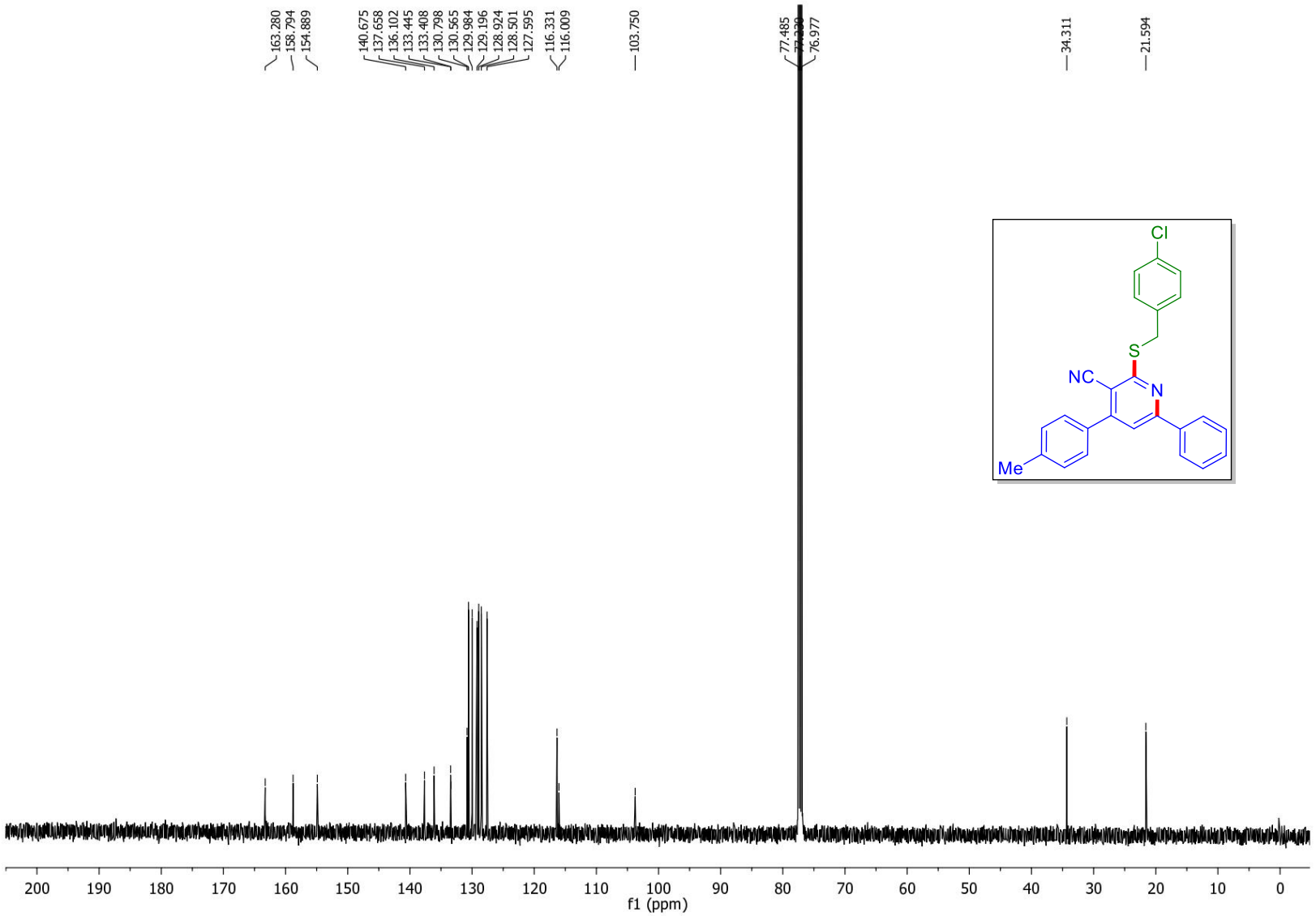
2-((4-Chlorobenzyl)thio)-4,6-diphenylnicotinonitrile (1n): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



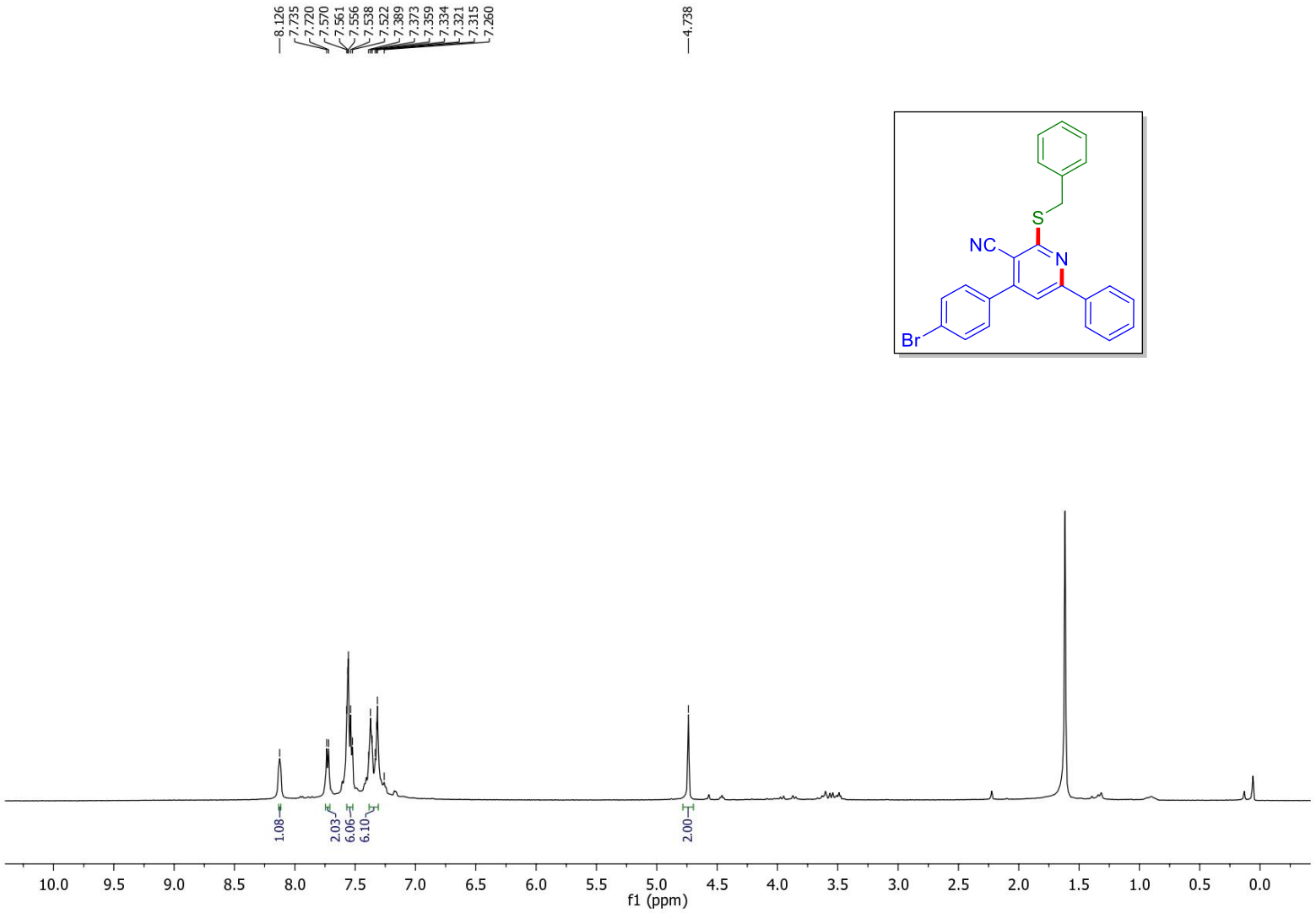
2-((4-Chlorobenzyl)thio)-6-phenyl-4-(p-tolyl)nicotinonitrile (2n): ^{1}H NMR (CDCl$_3$, 500 MHz)



2-((4-Chlorobenzyl)thio)-6-phenyl-4-(p-tolyl)nicotinonitrile (2n): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



2-(Benzylthio)-4-(4-bromophenyl)-6-phenylnicotinonitrile (6o): ^{1}H NMR (CDCl$_3$, 500 MHz)



2-(Benzylthio)-4-(4-bromophenyl)-6-phenylnicotinonitrile (6o): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)