Supporting Information

Sequential Multiple C–H Activation Enabled Modular Construction of Polyfunctional Sulfur-Contained Arenes

Wensen Ouyang, Xiaoqing Cai, Xiaojian Chen, Jie Wang, Jianhang Rao, Yang Gao, Yanping Huo, Qian Chen, Xianwei Li*

School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou, 510006, China.

E-mail: xwli@gdut.edu.cn

Table of Contents

A. General Information

^{1}H and ^{13}C NMR spectra were recorded on BRUKER DRX-400 spectrometer using $CDCl_3$ as solvent and TMS as an internal standard. Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 7.26, singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet); dt (doublets of triplet); dq (doublets of quartet). Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 77.0, triplet). Gas chromatograph mass spectra were obtained with a SHIMADZU model GCMS–QP 5000 spectrometer. HRMS was carried out on a MAT 95XP (Thermo).

B. General procedure:

1) General procedure for the synthesis of arylimidates:

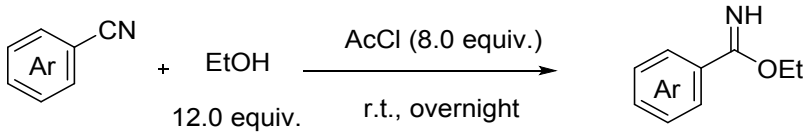


Figure S1. Synthesis of arylimidates.

To a stirred solution of a nitrile (1.0 equiv.) and an alcohol (12.0 equiv.), AcCl was added (8.0 equiv.) dropwise at 0 ºC. The Schlenk tube was stoppered tightly and the stirring was continued at 25 ºC. After the reaction was complete monitored by TLC, the volatiles were removed under reduced pressure to isolate the benzimidate hydrochloride. Then slowly mixed benzimidate hydrochloride and saturated aqueous $NaHCO_3$ solution inice bath, until gas evolution had ceased. The product was extracted into Et_2O and the organic solution was washed with H_2O and brine and concentrated under reduced pressure to obtain the benzimidates. The procedure was according to the reference: Yadav, V. K.; Babu, K. G. A Remarkably Efficient Markovnikov Hydrochlorination of Olefins and Transformation of Nitriles into Imidates by Use of AcCl and an Alcohol. *Eur. J. Org. Chem*. **2005**, 452.

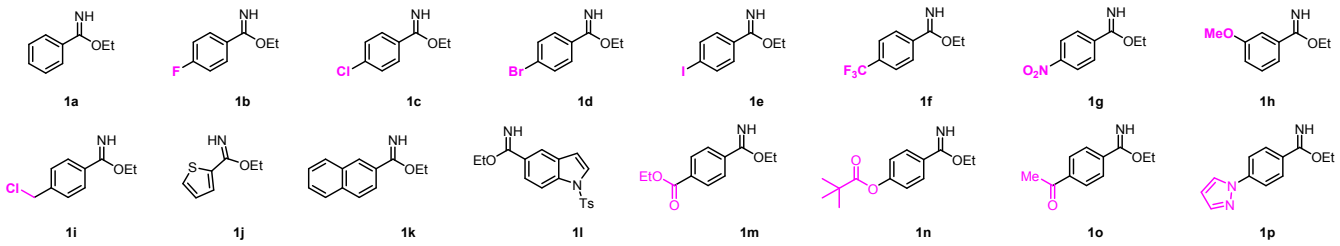


Figure S2. Imidate ester substrates

2) Synthesis of disulfides-1:

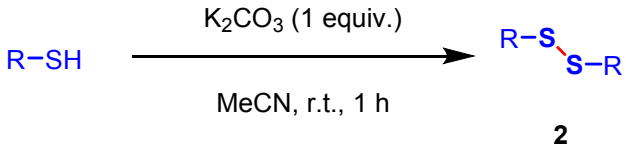


Figure S3. Synthesis of disulfides from thiols.

To a round bottle (50 mL) were added thiophenol (5 mmol), anhydrous potassium carbonate (0.69 g, 5 mmol), and MeCN (10 mL) sequentially, and the reaction was conducted at room temperature under air atmosphere for 1 hour. And the desired disulfides were obtained quantitatively, after filter and concentration.

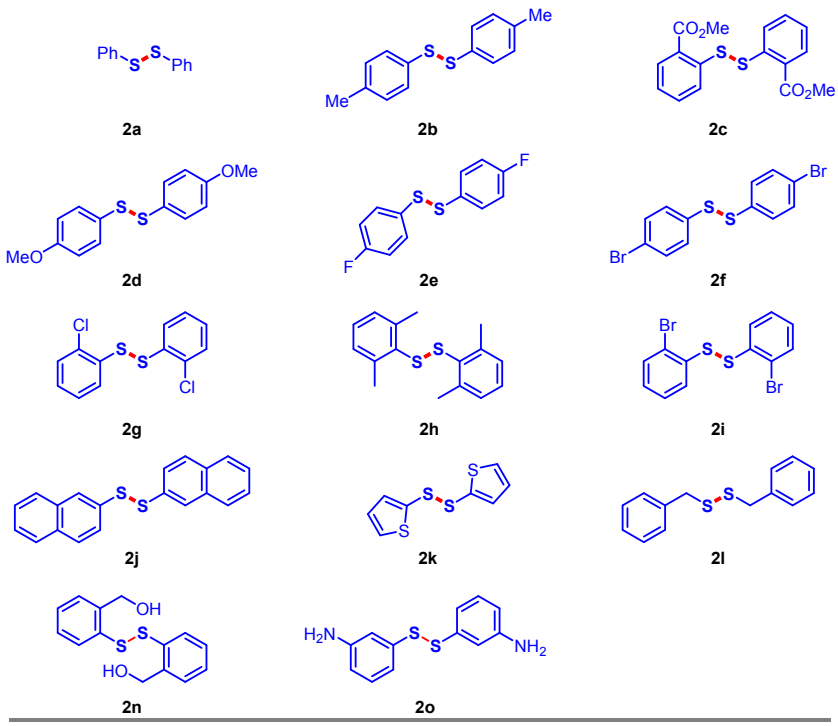


Figure S4. Disulfide substrates-1.

Synthesis of disulfides-2:

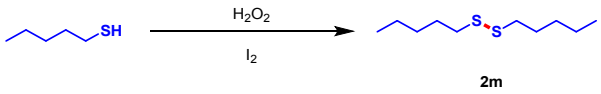
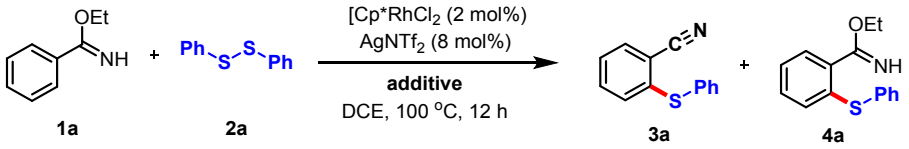


Figure S5. Disulfide substrates-2.

A round bottom flask was charged with 1% H_2O_2 (1 mmol) and I_2 (0.01 mmol). The thiol (1 mmol) was added to the solution at room temperature with vigorous stirring. The reaction was monitored by TLC (n-hexane:ethyl acetate 15:3). After the completion of the reaction, the products were filtered off and dried or extracted with ethyl acetate (3 × 5 mL). Then the combined organic phases were washed with water (2 × 4 mL), separated, and dried with anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to obtain the corresponding disulfides.

3) Optimization of reaction conditions.

Table S1. Variations from standard conditions for switchable C-H sulfenylation[a]

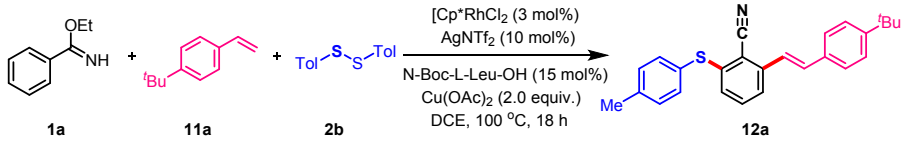


1a **2a** **3a** **4a**

Entry	Variations from standard conditions	Yield[b] (%) **3a**	**4a**
1	**$Cu(OAc)_2$ (2.0 equiv.)** as the additive	**82**	< 10
2	**AgOAc (1.5 equiv.)** as the additive	< 10	**71**
3	$[Ru(p\text{-cymene})Cl_2]_2$ as the catalyst	73[c]	56[d]
4[c]	$[Cp^*IrCl_2]_2$ as the catalyst	-	-
5[c]	$Pd(OAc)_2$ as the catalyst	-	-
6[c]	$NiBr_2$ as the catalyst	-	-
7[c]	without $[RhCp^*Cl_2]_2$	-	-
8[c]	without $AgNTf_2$	43	31
9[c]	$AgSbF_6$ instead of $AgNTf_2$	< 10	< 10
10[c]	HOAc or PivOH instead of NaOAc	< 10	< 10
11	without $Cu(OAc)_2$	< 10	< 10
12	O_2 (1 atm) instead of $Cu(OAc)_2$	< 10	< 10
13[c]	**PhSH** instead of **2a**	36	25
14[c]	acetone or ^{t}BuOH as the solvent	trace	trace

[a] Standard conditions: **1a** (0.3 mmol), **2a** (0.3 mmol), $[Cp^*RhCl_2]_2$ (2 mol%), $AgNTf_2$ (5 mol%), $Cu(OAc)_2 \cdot H_2O$ (2.0 equiv.), DCE (1 mL), 100 °C, 12 h. [b] Isolated yield. [c] with $Cu(OAc)_2 \cdot H_2O$ (2.0 equiv.). [d] with AgOAc (1.2 equiv.).

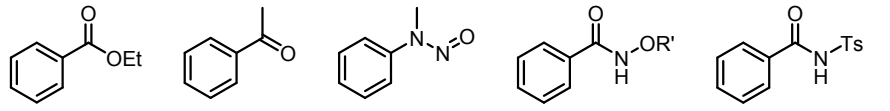
Table S2. Exploration of reaction conditions for sequential C–H activation. [a]



1a **11a** **2b** **12a**

Entry	Variations from standard conditions	Yield[b] (%)
1	None	73
2	$[Ru(p\text{-cymene})Cl_2]_2$ as the catalyst	41
3	$[Cp^*IrCl_2]_2$ as the catalyst	n.r.
4	$Pd(OAc)_2$ as the catalyst	n.r.
5	$NiBr_2$ as the catalyst	n.r.
6	without $[RhCp^*Cl_2]_2$	n,r
7	without $AgNTf_2$	< 10
8	HOAc instead of N-Boc-L-Leu-OH	< 10
9	PivOH instead of N-Boc-L-Leu-OH	< 10
10	without $Cu(OAc)_2{\cdot}H_2O$	trace
11	O_2 (1 atm) instead of $Cu(OAc)_2{\cdot}H_2O$	< 10
12	**Tol-SH** instead of **2b**	17
13	60 °C	36
14	acetone or ^{t}BuOH as the solvent	trace

Unsuccessful directing groups:



1a-1, n.r. **1a-2**, n.r. **1a-3**, n.r. **1a-4**, R' = Me, n.r. **1a-5**, R' = Piv, n.r. **1a-6**, n.r.

[a] Conditions: **1a** (0.30 mmol), **11a** (0.45 mmol), **2b** (0.45 mmol), $[RhCp^*Cl_2]_2$ (3 mol%), $AgNTf_2$ (10 mol%), N-Boc-L-Leu-OH (15 mol%), $Cu(OAc)_2{\bullet}H_2O$ (2.0 equiv.), DCE (2 mL), 100 °C, 12 h. [b] Isolated yield. n.r. = no reaction.

For esters, ketones, N-nitroso aniline, no reactivity was observed for the C–H sulfenylation in this sequential C–H activation. For N-OMe or N-OPiv amides **1a-4** or **1a-5** in this multiple C–H activation, only oxidative Heck reaction was observed, while no further C–H sulfenylation was obtained.

Notably, N–Ts benzamide **1a-6** exhibited no reactivity in this sequential multiple C–H activation, and polyfunctional arene **12a-6-1** or thioether substituted isoindolin-1-one **12a-6-2**, were not observed (**Firgure S6**). Although N–Ts amide directed C–H sulfenylation (C. Liu, Y. Fang, S.-Y. Wang, S.-J. Ji, *Org. Lett*., **2018**, *20*, 6112−6116.) or assisted oxidative olefination/cyclization (S. W. Youn, T. Y. Ko, Y. H. Kim, Y. A. Kim, *Org. Lett*., **2018**, *20*, 7869−7874.) was reported, respectively.

Moreover, control experiment using **1a-6′**, derived from oxidative olefination/cyclization of N-Ts amide with substituted styrene, exhibited no reactivity for the further C–H sulfenylation with disulfide **2b′** under this standard conditions using Rh(III) catalysis. It was speculated that the existence of N-H of N-Ts benzamide was crucial for the subsequent C-H activation under metal catalysis.

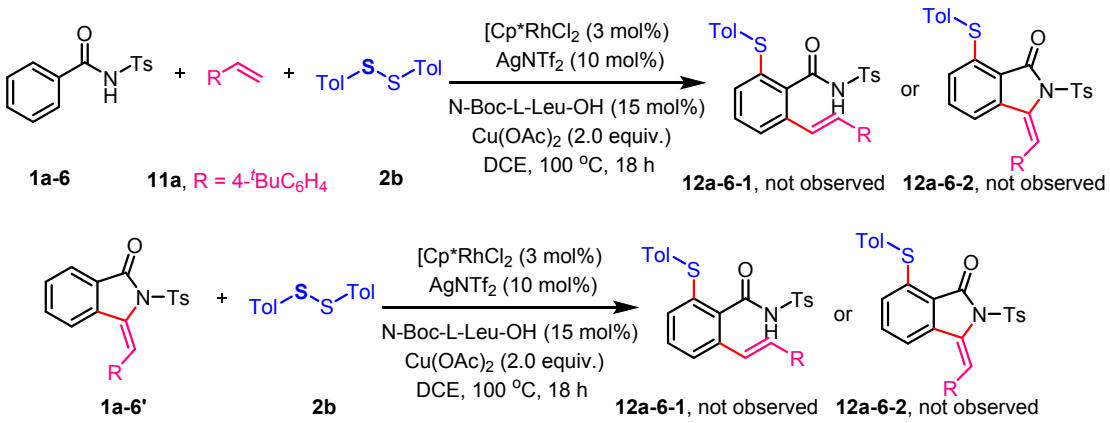


Figure S6. Attempts for N–Ts benzamides assisted sequential C–H activation.

Further investigation of reaction conditions revealed that: 1) the amount of Cu(II) salt could be reduced to 1 equiv., with the addtion of benzoquinone (Figure S7, eq. 1);

2) Multiple dehydrogenative coupling served as an expedient arena for concise delivery of polyfunctional molecules, along this line, we also conducted experiments by direct use Tol-SH instead of disufide **2b** under standard conditions via Rh(III) catalysis (Figure S7, eq. 2), and the desired product **12a** was obtained in low yield.

3) Inspired by Glorius's work (T. Gensch, F. J. R. Klauck, F. Glorius, *Angew. Chem. Int. Ed.*, **2016**, *55*, 11287–11291.), further attempts for the sequential C–H activation under Co(III) catalysis were also conducted (Figure S7, eq. 3). Primary investigation indicated that ~30% yield of the desired polyfunctional arene product **12a** could be obtained. Further optimization of this sequential multiple dehydrogenative coupling was underway.

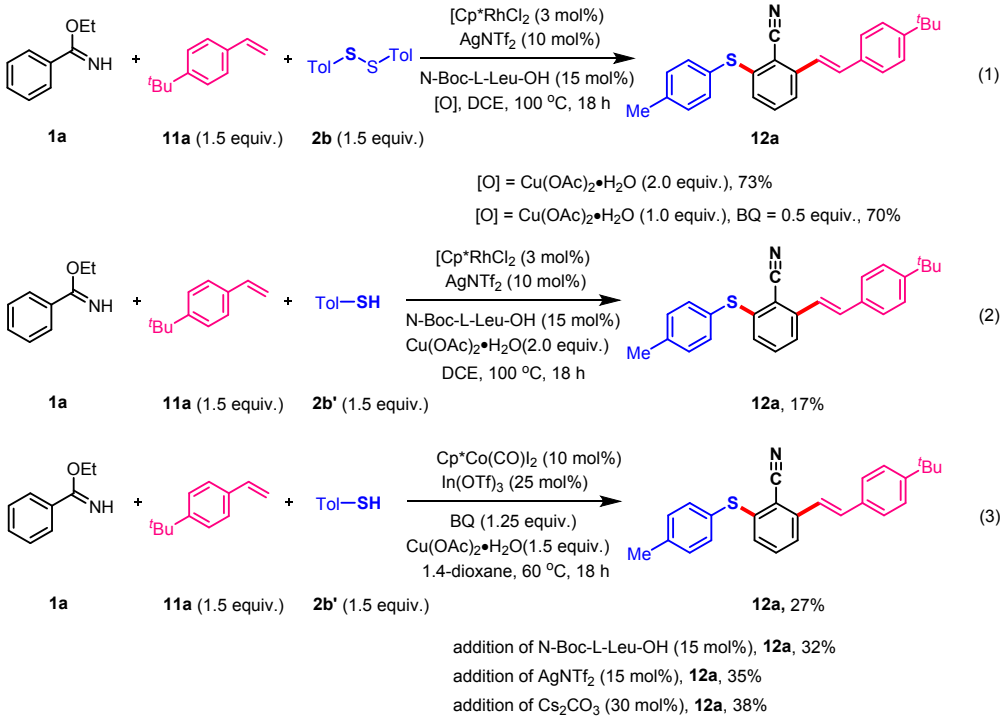


Figure S7. Further investigations for sequential C–H activation.

4) General procedure for the synthesis of *ortho*-thioether aryl nitriles 3:

An oven-dried 10 mL Schlenk Tube was charged with imidates **1** (0.30 mmol), $[RhCp^*Cl_2]_2$ (0.002 mmol), $AgNTf_2$ (0.008 mmol) and $Cu(OAc)_2•H_2O$ (2.0 equiv.) in sequence, followed by addition of disulfides **2** (0.45 mmol) in DCE (1.0 mL) through syringe. The resulting reaction mixture was stirred at 100 ºC for 12 h and then diluted with CH_2Cl_2 and filtered through diatomite. Removing the solvent in vacuo and purification of the residue by silica gel column chromatography afforded the desired products **3**.

For the synthesis of thioethers 4:

An oven-dried 10 mL Schlenk Tube was charged with imidates **1** (0.30 mmol), $[RhCp^*Cl_2]_2$ (0.002 mmol), $AgNTf_2$ (0.008 mmol) and AgOAc (1.2 equiv.) in sequence, followed by addition of disulfides **2** (0.45 mmol) in DCE (1.0 mL) through syringe. The resulting reaction mixture was stirred at 100 ºC for 12 h and then diluted with CH_2Cl_2 and filtered through diatomite. Removing the solvent in vacuo and purification of the residue by silica gel column chromatography afforded the desired products **4**.

5) General procedure for the three component synthesis of multiple functionalized thioethers: synthesis of multiple functionalized thioethers 12:

An oven-dried 10 mL Schlenk Tube was charged with imidates **1** (0.3 mmol), $[RhCp^*Cl_2]_2$ (0.003 mmol), $AgNTf_2$ (0.01 mmol), N-Boc-L-Leu-OH (15 mol%) and in sequence, followed by addition of terminal olefins **11** (0.45 mmol) in DCE (1.0 mL) through syringe. The resulting reaction mixture was stirred at 100 ºC for 12 h. And then, $Cu(OAc)_2·H_2O$ (2.0 equiv.), disulfides **2** (0.45 mmol) in DCE (0.5 mL) was inserted into the reaction system through syringe for another 12 hours. After that, the reaction mixture was diluted with CH_2Cl_2 and filtered through diatomite. Removing the solvent in vacuo and purification of the residue by silica gel column chromatography afforded the desired products **12**.

For the synthesis of multiple functionalized thioethers 14:

An oven-dried 10 mL Schlenk Tube was charged with imidates **1** (0.3 mmol), $[RhCp^*Cl_2]_2$ (0.003 mmol), $AgNTf_2$ (0.01 mmol), N-Boc-L-Leu-OH (15 mol%) in sequence, followed by addition of terminal alkenes **11** (0.45 mmol) in DCE (1.0 mL) through syringe. The resulting reaction mixture was stirred at 100 ºC for 12 h; And then, AgOAc (1.2 equiv.), disulfides **2** (0.45 mmol) in DCE (0.5 mL) was inserted into the reaction system through syringe for another 12 hours. After that, the reaction mixture was diluted with CH_2Cl_2 and filtered through diatomite. Removing the solvent in vacuo and purification of the residue by silica gel column chromatography afforded the desired products.

C. Synthetic applications

1) Sequential C–H sulfenylation and arylation: synthesis of 9

An oven-dried 10 mL Schlenk Tube was charged with imidates **1a** (0.10 mmol), $[RhCp^*Cl_2]_2$ (0.002 mmol), $AgNTf_2$ (0.008mmol), $Cu(OAc)_2 \cdot H_2O$ (2.0 equiv.) in sequence, followed by addition of disulfides **3i** (0.15 mmol) in DCE (1.0 mL) through syringe. The resulting reaction mixture was stirred at 100 ºC for 12 h and then diluted with CH_2Cl_2 and filtered through diatomite. Removing the solvent in vacuo and purification of the residue by silica gel column chromatography afforded the desired product **3t**.

With product **3t** (0.3 mmol), $PdCl_2(PPh_3)_2$ (0.006 mmol), KOPiv (2 equiv.) in DMA (*N*,*N*-dimethyl acetamide) (1 mL) in an oven-dried Schlenk tube under 140 °C, and the reaction was conducted for 12 hours. After reaction finished, the solution was washed with brine (20 mL × 2), and extracted with ethyl acetate (20 mL × 2), and obtained solution was concentrated and purification of the residue by silica gel column chromatography afforded the desired product **9** (**Figure S8**).

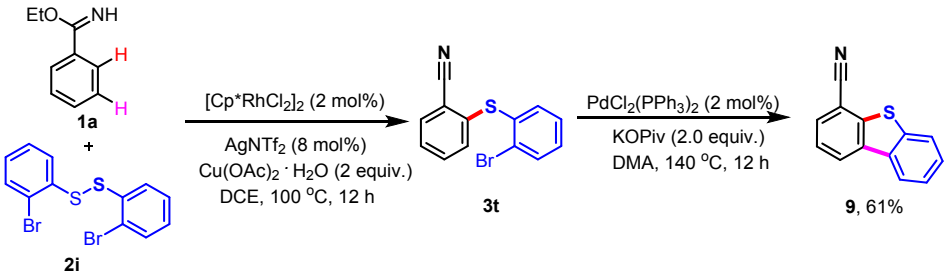


Figure S8. Sequential C-H activation: synthesis of dibenzo[b,d]thiophene-4-carbonitrile 9

2) Expedient delivery of Bipenamol:

Synthesis of intermediate 3zf:

An oven-dried 10 mL Schlenk Tube was charged with imidates **1a** (0.1 mmol), $[RhCp^*Cl_2]_2$ (0.002 mmol), $AgNTf_2$ (0.008 mmol) and $Cu(OAc)_2 \cdot H_2O$ (2.0 equiv.) in sequence, followed by addition of disulfides **2n** (0.15 mmol) in DCE (1.0 mL) through syringe. The resulting reaction mixture was stirred at 100 ºC for 12 h. After that, the reaction mixture was diluted with CH_2Cl_2 and filtered through diatomite. Removing the solvent in vacuo and purification of the residue by silica gel column chromatography afforded the desired product **3zf**.

Synthesis of Bipenamol 10:

To a round bottle was added product **3zf** (0.2 mmol) in THF (2 mL), which was further added $LiAlH_4$ (4 equiv.), the obtained solution was heated to 120 °C for 10 minutes. After the reaction was cooled to room temperature, water (20 mL) was added, and the reaction mixture was extracted with ethyl acetate and filtered through diatomite. Removing the solvent in vacuo and purification of the residue by silica gel column chromatography afforded the desired product **10** (**Figure S9**).

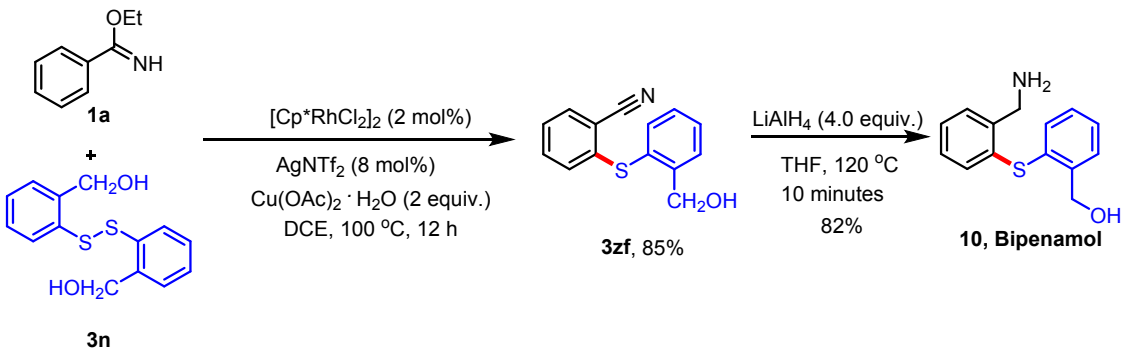


Figure S9. Concise synthesis of Bipenamol

3) Further transformation of polyfunctional arene products 12a:

1) To an ice-cold, stirred solution of **12a** (0.2 mmol) in DMSO (0.4 mL), 30% H_2O_2 and anhyd K_2CO_3 (20 mg) were added. The mixture was allowed to warm to r.t. After 1 hour, H_2O (1.5 mL) was added, the product isolated by filtration and dried to yield the desired product **12a-1**.

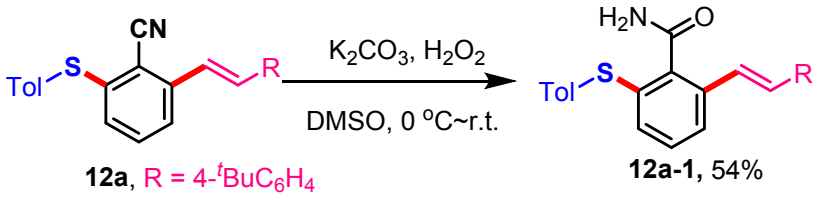


Figure S10. Transformation of aryl nitrile product 12a to the amide 12a-1

2) To a solution of **12a** (0.2 mmol) in THF (2 mL) was dropped CH_3MgBr (3.0 M solution in Et_2O, 0.3 mmol, 0.1 mL) and refluxed for 12 h under nitrogen atmosphere. After completion of the reaction, the solvent was removed under reduced pressure. After addition of hydrochloric acid (1 mL, 4M), the mixture was refluxed for another 4 h. The mixture was cooled to room temperature and extracted with toluene (4 mL, 3 times). The combined organic layers were washed with water, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give **12a-2** as yellowish oil.

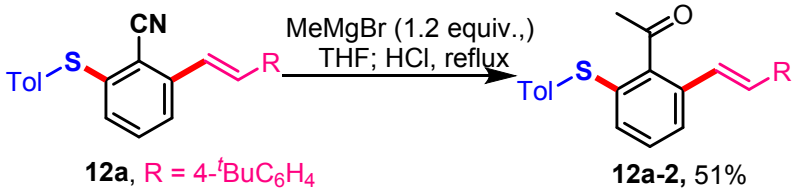


Figure S11. Transformation of aryl nitrile product 12a to the ketone 12a-2

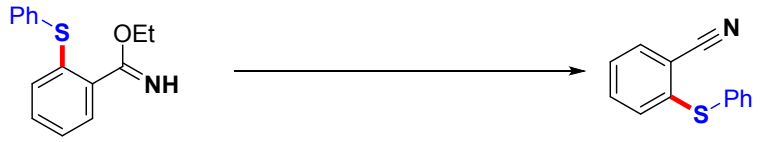
D. Preliminary mechanism studies:

To obtain some insight into this multiple cascade reaction, we conducted the following experiments:

1) Conversion of thioether product **4a** to **3a (Figure S12)**:

To elucidate the role of metal salts such as AgOAc and $Cu(OAc)_2•H_2O$ for the generation of imidate ester or nitrile substituted thioethers, first, we found that product **3a** could be obtained in high efficiency under standard conditions. Control experiments revealed that $Cu(OAc)_2•H_2O$ was crucial for the conversion of product **4a** to **3a**, while air or AgOAc exhibited low conversion.

These observations indicated that Cu(II) salt was essential for the generation of nitrile substituted aryl thioethers. It was speculated that silver exhibited stronger Lewis acidity, which might favor the imidate ester functionality remained intact, while Cu(II) salt might promote the release of ethol moiety from the corresponding imidate ester products.



4a **3a**

Conditions	Yield
standard conditions	81%
$Cu(OAc)_2 \cdot H_2O$ (30 mol%), air, DCE, 100 °C, 12 h	87%
air, DCE, 100 °C, 12 h	11%
AgOAc (1.5 equiv), DCE, 100 °C, 12 h	12%

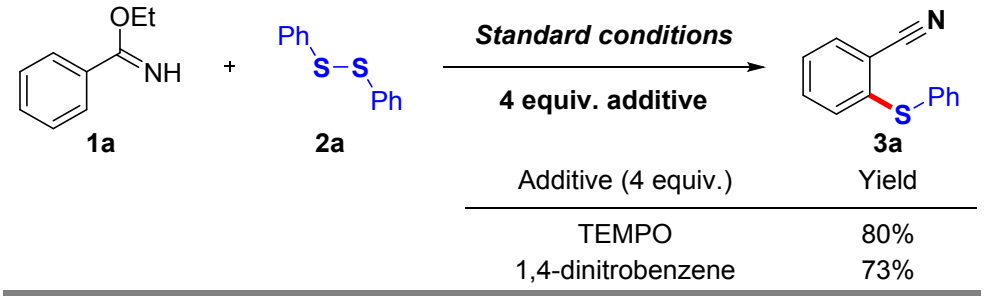
Standard conditions: **4a** (0.1 mmol), $[Cp^*RhCl_2]_2$ (2 mol%), $AgNTf_2$ (5 mol%) $Cu(OAc)_2 \cdot H_2O$ (2.0 equiv.), DCE (1 mL), 100 °C, 12 h.

Figure S12. Conversion of **4a** to **3a**

2) To gain some insight into this transformation that if radical process was involved, some radical-scavenger studies were conducted.

Procedure: To a 25 mL Schlenk tube equipped with a magnetic stirring bar was added the substrate **1a** (0.1 mmol), $[RhCp^*Cl_2]_2$ (2.5 mg, 0.002 mmol), $AgNTf_2$ (0.008 mmol) and $Cu(OAc)_2 \cdot H_2O$ (2.0 equiv.) in sequence under N_2 atmosphere, followed by addition of disulfide PhSSPh **2a** (25.0 mg, 0.15 mmol) in DCE (1.0 mL) through syringe. The tube was capped, and heated to 100 °C for 12 h. After cooled to room temperature, the reaction mixture was filtered through a pad of Celite. The filtrate was concentrated in vacuo to afford crude product, which was analyzed with ^1H NMR using CH_2Br_2 as the internal standard.

The results revealed that radical or an electron scavenger TEMPO and 1,4-dinitrobenzene showed no significant inhibition for the generation of the desired thioether product **3a**. These experiments indicated that single-electron transfer (SET) pathway might not be involved in this transformation (**Figure S13**).



Additive (4 equiv.)	Yield
TEMPO	80%
1,4-dinitrobenzene	73%

Figure S13. Radical-trapping experiment

3) According to the literatures and experimental observations, a tentative mechanism was proposed in **Figure S14**. It was speculated that coordination of imidate ester with Rh(III) took place to initate this transformation, which followed by C–H activation to give the key 5-membered rhodacycle intermediate **A**. Subsequent nucleophic substitution with disulfide **3a**, giving to the desired *ortho* C-H sulfenylation product **3a** or **4a** (**path a**), depending on the Ag(I) or Cu(II) salt added to the reaction system, together with rodium intermediate **B-1**. According to the control experiments depicted in **Figure S9**, the in situ generated ortho imidate ester substituted aryl thioethers **9** could also converted to the thioethers **8**. Further reaction of intermediate B with imidate ester substrate 1a led to Rh(III) species D, which underwent reductive elimination to afford the desired thioether products **3a** or **4a**, and the released Rh(I) species was re-oxidzed to reactive Rh(III) catalyst by Ag(I) or Cu(II).

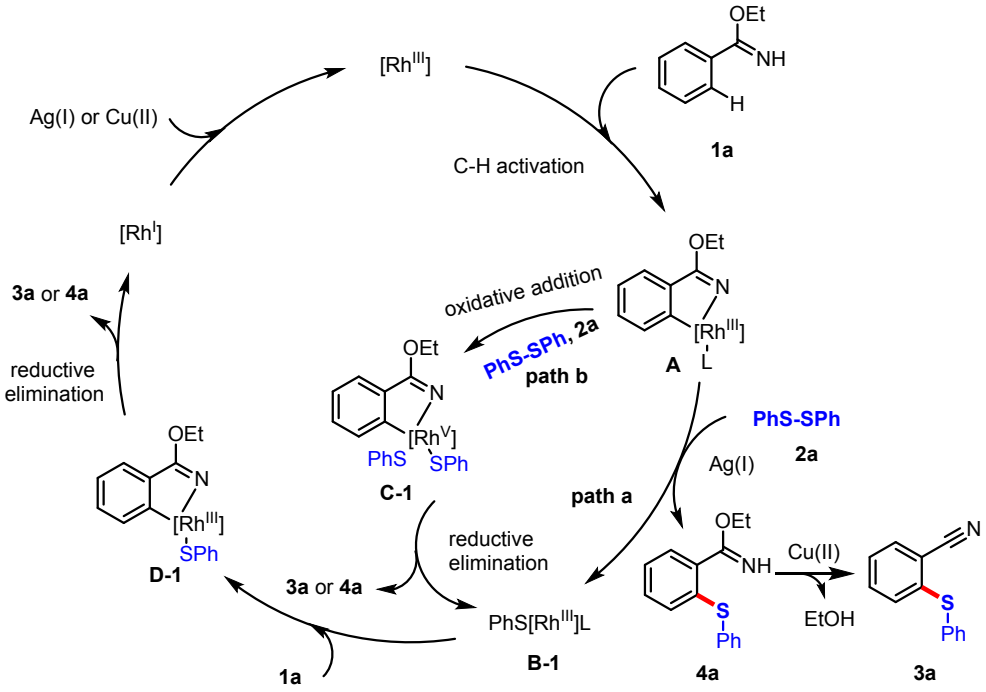


Figure S14. Proposed Mechanism for the Divergent Construction of thioethers.

Alternatively, the in situ generated 5-membered rhodacycle intermediate A might undergo oxidative addition with disulfide **3a** to give Rh(V) intermediate **C**, which followed by reductive elimination to give the desired product **3a** or **4a** and rhodium species **B-1.**

For the multiple C-H activation reactions, a tentative mechanism was proposed (**Figure S15**). First, with the assistance of mono-N-protected amino acid (MPAA), C–H activation of imidate ester **1a** took place, to give rhodacycle species **A**. Subsequent oxidative Heck reaction led to intermediate **C** or **C'** via second C-H activation, which facilitated further reaction with sulfide species **D** generated from disulfide **2**, affording to key intermediate **E**. Finally, the desired multiple C–H activation products **12** or **14** were released via C–S bond reductive elimination, and reoxidation of the released Rh(I) species by Ag(I) or Cu(II) oxidant. When with key intermediate **C**, dual cross-dehydrogenative coupling reaction of imidate ester with arene and terminal olefins, could also proceed with the assistance of PivOH and oxidant, affording to products **15**.

Notably, when disulfides **2** were subjected into reaction prior to terminal olefins **11**, C–H sulfenylation took place to give **4**. However, the overcoordination of imidate ester and thioether group to Rh(III) led to deactivation of Rh(III) catalyst, and thus, no second C–H activation proceed.

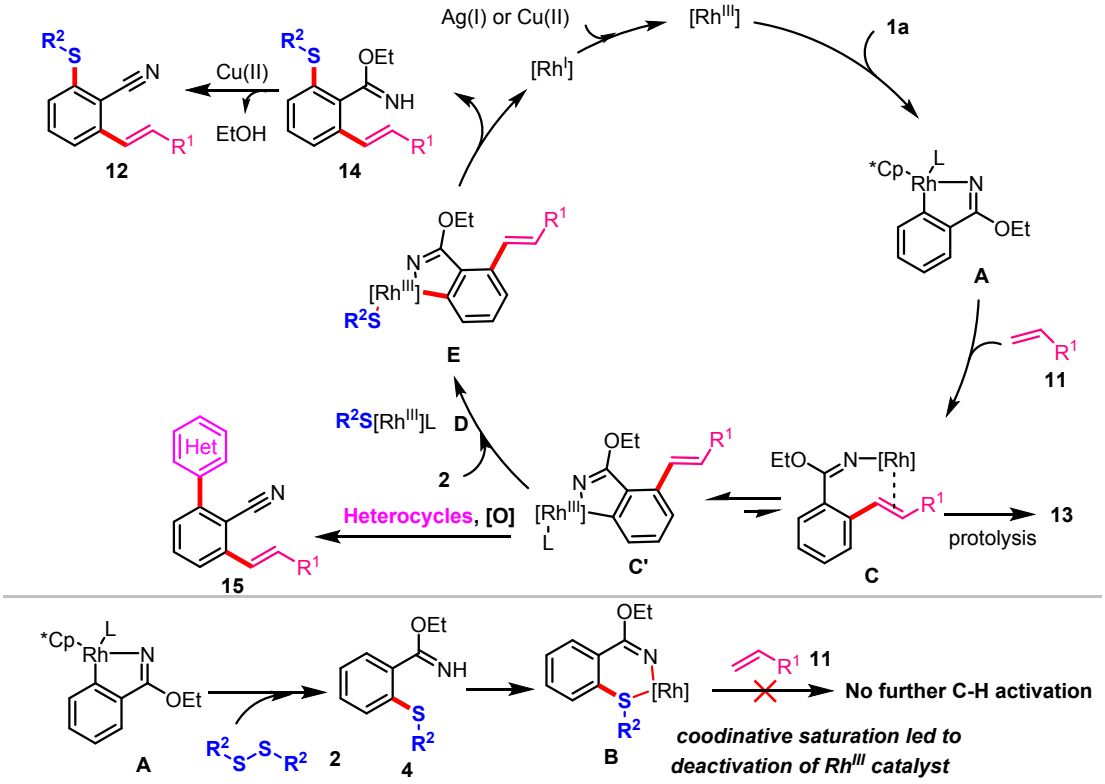
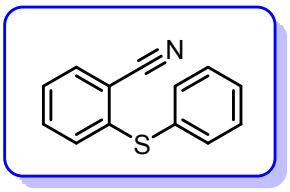
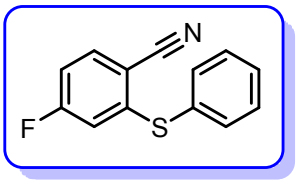


Figure S15. Proposed Mechanism.

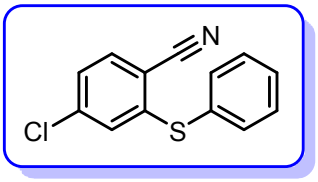
E. Analytical data for the obtained products:



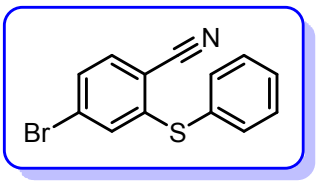
2-(Phenylthio)benzonitrile (3a),[1] **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.40 (dd, *J* = 1.2 Hz, 7.6 Hz, 1H), 7.49-7.46 (m, 2H), 7.43-7.38 (m, 4H), 7.28-7.25 (m, 1H), 7.13 (dd, *J* = 0.4 Hz, 8.0 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 142.3, 133.6, 133.5, 132.9, 131.8, 129.9, 129.7, 128.9, 126.4, 116.9, 112.9.



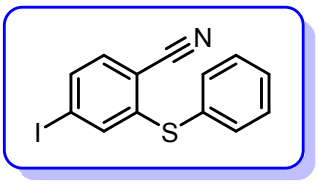
4-Fluoro-2-(phenylthio)benzonitrile (3b), **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.62 (dd, *J* = 5.2 Hz, 8.4 Hz, 1H), 7.55-7.53 (m, 2H), 7.48-7.46 (m, 3H), 6.90 (td, *J* = 2.8 Hz, 8.0 Hz, 1H), 6.63 (dd, *J* = 2.4 Hz, 9.2 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 165.1 (d, *J* = 258.0 Hz), 147.2 (d, *J* = 9.0 Hz), 135.7 (d, *J* = 10.0 Hz), 134.8, 130.2, 130.0, 129.8, 116.2, 115.5 (d, *J* = 26.0 Hz), 113.7 (d, *J* = 23.0 Hz), 107.3. **^{19}F NMR (300 MHz, $CDCl_3$) δ** -101.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_9FNS$: 230.0434, Found: 230.0430.



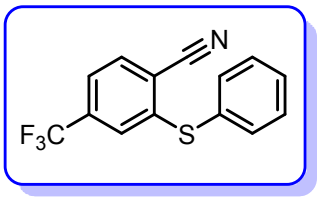
4-Chloro-2-(phenylthio)benzonitrile (3c), **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.61-7.59 (m, 1H), 7.55-7.51 (m, 2H), 7.48-7.44 (m, 3H), 7.19 (dd, *J* = 2.0 Hz, 8.4 Hz, 1H), 6.96 (d, *J* = 2.0 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 145.3, 1398, 134.4, 133.4, 130.1, 129.8, 129.7, 128.5, 126.5, 116.1, 110.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_9ClNS$: 246.0139, Found: 246.0137.



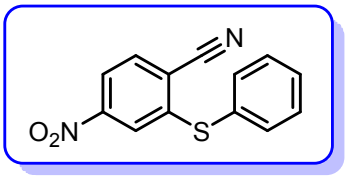
4-Bromo-2-(phenylthio)benzonitrile (3d),[2] **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.53-7.50 (m, 2H), 7.48-7.44 (m, 4H), 7.36 (dd, *J* = 2.0 Hz, 8.0 Hz, 1H), 6.96 (d, *J* = 2.0 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 145.1, 134.4, 134.3, 131.5, 130.1, 129.7, 129.4, 128.2, 127.7, 116.2, 110.6.



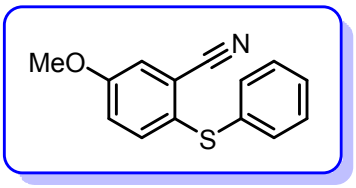
4-Iodo-2-(phenylthio)benzonitrile (3e), **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.59-7.50 (m, 3H), 7.48-7.44 (m, 4H), 7.14 (d, J = 1.6 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 145.2, 134.4, 134.3, 131.5, 130.5, 130.1, 129.7, 129.4, 128.2, 116.2, 110.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_9INS$: 337.9495, Found: 337.9498.



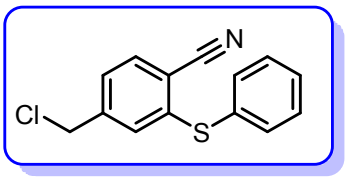
2-(Phenylthio)-4-(trifluoromethyl)benzonitrile (3f),[3] yellow solid, m. p. 81-84°C. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.75 (d, J = 8.0 Hz, 1H), 7.54-7.52 (m, 2H), 7.48-7.45 (m, 4H), 7.23 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 145.1, 134.8 (q, J = 34.0 Hz), 134.4, 134.1, 130.2, 129.9, 125.3 (q, J = 4.0 Hz), 122.6 (q, J = 4.0 Hz), 122.7 (q, J = 272.0 Hz), 121.4, 115.7, 115.0. **^{19}F NMR (300 MHz, $CDCl_3$) δ** -63.7.



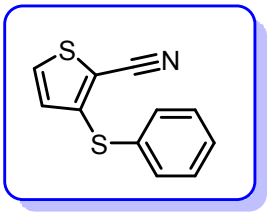
4-Nitro-2-(phenylthio)benzonitrile (3g), **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.00 (dd, J = 2.0 Hz, 8.4 Hz, 1H), 7.80 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 2.0 Hz, 1H), 7.59-7.57 (m, 2H), 7.54-7.51 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 150.2, 147.3, 135.0, 134.5, 133.4, 130.5, 128.6, 124.3, 122.2, 120.1, 116.0, 115.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_9N_2O_2S$: 257.0379, Found: 257.0383.



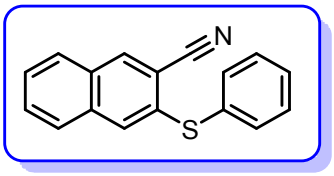
5-Methoxy-2-(phenylthio)benzonitrile (3h), **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.38 (d, J = 8.8 Hz, 1H), 7.30 (d, J = 4.4 Hz, 4H), 7.27-7.24 (m, 1H), 7.17 (d, J = 3.2 Hz, 1H), 7.05 (dd, J = 2.8 Hz, 8.8 Hz, 1H), 3.83 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 159.2, 135.4, 135.1, 130.7, 130.2, 129.4, 127.5, 120.0, 118.4, 117.3, 117.0, 55.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{12}NOS$: 242.0634, Found: 242.0632.



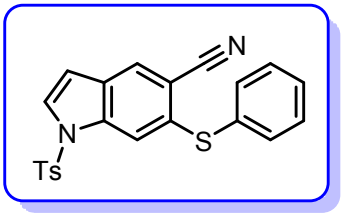
4-(Chloromethyl)-2-(phenylthio)benzonitrile (3i), **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.63 (d, J = 8.0 Hz, 1H), 7.52-7.48 (m, 2H), 7.43-7.41 (m, 3H), 7.28 (dd, J = 1.6 Hz, 8.0 Hz, 1H), 7.10 (d, J = 1.2 Hz, 1H), 4.43 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 143.2, 142.7, 133.9, 133.7, 132.5, 131.1, 129.9, 129.2, 129.1, 126.4, 116.5, 112.3, 44.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{11}ClNS$: 260.0295, Found: 260.0292.



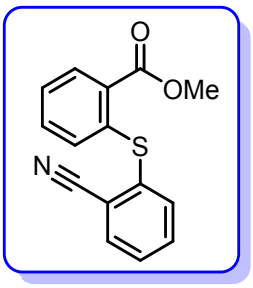
3-(Phenylthio)thiophene-2-carbonitrile (3j), **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.48 (d, J = 5.2 Hz, 1H), 7.46-7.43 (m, 2H), 7.38-7.35 (m, 3H), 6.80 (d, J = 5.2 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 145.1, 132.7, 132.3, 131.9, 129.9, 129.6, 128.6, 113.0, 106.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{11}H_8NS_2$: 218.0093, Found: 218.0090.



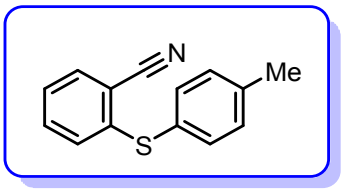
3-(Phenylthio)-2-naphthonitrile (3k),[4] **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.25 (s, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.76 (s, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.63-7.54 (m, 2H), 7.45 (dd, J = 2.4 Hz, 8.0 Hz, 2H), 7.40-7.34 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 136.1, 134.9, 134.1, 133.4, 132.2, 131.2, 131.0, 129.6, 128.2, 128.16, 127.6, 127.5, 117.2, 112.3.



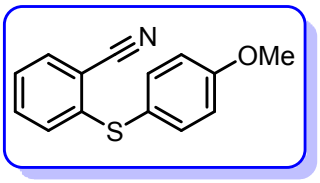
6-(Phenylthio)-1-tosyl-1*H*-indole-5-carbonitrile (3l), **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.84 (d, J = 13.2 Hz, 2H), 7.62 (d, J = 3.6 Hz, 1H), 7.52 (d, J = 8.4 Hz, 2H), 7.45-7.43 (m, 5H), 7.20 (d, J = 8.4 Hz, 2H), 6.64 (d, J = 3.2 Hz, 1H), 2.38 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 145.7, 136.6, 136.5, 134.3, 133.0, 130.1, 129.7, 129.3, 128.6, 128.5, 127.5, 127.0, 117.4, 116.3, 109.1, 108.1, 21.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{17}N_2O_2S_2$: 405.0726, Found: 405.0723.



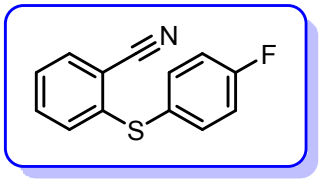
Methyl 2-((2-cyanophenyl)thio)benzoate (3m), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.98 (dd, J = 1.6 Hz, 8.0 Hz, 1H), 7.76-7.74 (m, 1H), 7.60-7.58 (m, 2H), 7.50-7.46 (m, 1H), 7.32-7.28 (m, 1H), 7.21 (dt, J = 1.2 Hz, 7.6 Hz, 1H), 6.79 (dd, J = 1.2 Hz, 8.0 Hz, 1H), 3.92 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.5, 139.3, 137.8, 135.8, 134.3, 133.4, 132.5, 131.2, 129.0, 128.4, 125.7, 118.1, 116.7, 52.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{12}NO_2S$: 270.0583, Found: 270.0581.



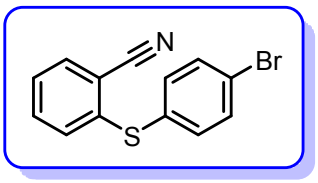
2-(*p*-Tolylthio)benzonitrile (3n),[4] **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.60 (dd, J = 1.2 Hz, 7.6 Hz, 1H), 7.41-7.35 (m, 3H), 7.23-7.18 (m, 3H), 7.03 (dd, J = 0.8 Hz, 8.0 Hz, 1H), 2.38 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.5, 139.6, 134.3, 133.5, 132.9, 130.6, 128.9, 127.6, 125.9, 125.0, 117.0, 111.9, 100.0, 21.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{12}NS$: 226.0685, Found: 226.0681.



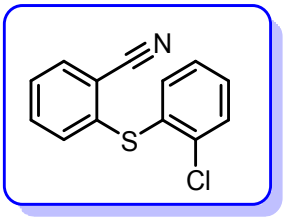
2-((4-Methoxyphenyl)thio)benzonitrile (3o),[5] **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.59 (d, J = 7.2 Hz, 1H), 7.48 (d, J = 8.4 Hz, 2H), 7.35 (td, J = 1.2 Hz, 8.0 Hz, 1H), 7.17 (t, J = 7.6 Hz, 1H), 6.97-6.92 (m, 3H), 3.85 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 160.8, 144.6, 136.8, 133.4, 132.8, 127.8, 125.4, 120.9, 117.0, 115.4, 110.9, 55.4.



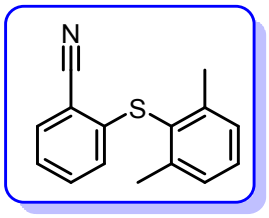
2-((4-Fluorophenyl)thio)benzonitrile (3p),[6] **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.64 (d, J = 8.0 Hz, 1H), 7.52-7.49 (m, 2H), 7.42 (t, J = 8.0 Hz, 1H), 7.28-7.24 (m, 1H), 7.13-7.07 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 163.3 (d, J = 250.0 Hz), 142.6, 136.2 (d, J = 8.0 Hz), 133.7, 133.0, 129.3, 126.7, 126.4, 117.1, 116.9, 116.8, 112.5. **^{19}F NMR (300 MHz, $CDCl_3$)** δ -111.17.



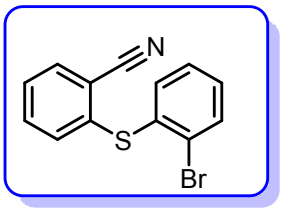
2-((4-Bromophenyl)thio)benzonitrile (3q),[6] **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 (dd, J = 1.6 Hz, 8.0 Hz, 1H), 7.53-7.49 (m, 2H), 7.45 (dt, J = 1.2 Hz, 8.0 Hz, 1H), 7.33-7.29 (m, 3H), 7.21 (dd, J = 0.4 Hz, 4.0 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 141.1, 134.5, 133.9, 133.1, 132.9, 131.6, 130.8, 127.1, 123.2, 116.8, 113.8.



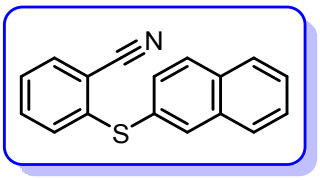
2-((2-Chlorophenyl)thio)benzonitrile (3r),[6] **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.68 (dd, J = 1.2 Hz, 7.6 Hz, 1H), 7.49-7.45 (m, 2H), 7.36-7.28 (m, 3H), 7.25 (dd, J = 1.6 Hz, 7.6 Hz, 1H), 7.22-7.19 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 139.5, 136.7, 133.9, 133.1, 131.3, 130.4, 129.8, 127.7, 127.3, 116.7, 114.3.



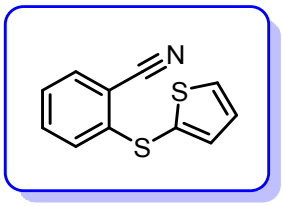
2-((2,6-Dimethylphenyl)thio)benzonitrile (3s), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.60 (d, J = 7.6 Hz, 1H), 7.31-7.27 (m, 2H), 7.22 (d, J = 7.2 Hz, 2H), 7.13 (t, J = 7.6 Hz, 1H), 6.52 (d, J = 7.6 Hz, 1H), 2.41 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 144.1, 143.5, 133.5, 132.9, 130.2, 128.8, 128.3, 125.1, 124.6, 116.9, 110.0, 21.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{14}NS$: 240.0841, Found: 240.0845.



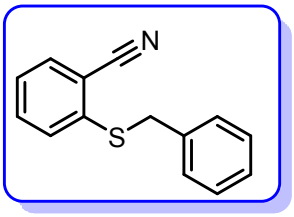
2-((2-Bromophenyl)thio)benzonitrile (3t),[6] **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.69 (dd, J = 7.6 Hz, 12.8 Hz, 2H), 7.48 (t, J = 7.2 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.28 (d, J = 4.0 Hz, 2H), 7.23-7.18 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 139.7, 134.2, 134.0, 133.8, 133.7, 133.2, 131.5, 129.7, 128.3, 127.4, 127.0, 116.7, 114.5.



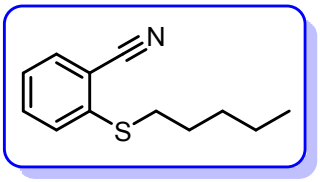
2-(Naphthalen-2-ylthio)benzonitrile (3u),[4] **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.01 (s, 1H), 7.83 (d, J = 8.8 Hz, 2H), 7.64 (d, J = 7.6 Hz, 1H), 7.53-7.51 (m, 2H), 7.45 (d, J = 8.4 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 7.12 (d, J = 8.0 Hz, 1H), 7.14 (d, J = 8.0 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 142.4, 133.8, 133.6, 133.3, 133.0, 132.9, 130.0, 129.9, 129.6, 128.9, 127.8, 127.7, 126.9, 126.4, 116.9, 112.7.



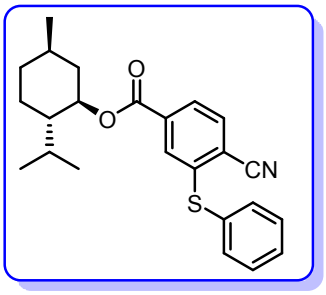
2-(Thiophen-2-ylthio)benzonitrile (3v),[6] **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.61-7.57 (m, 2H), 7.43-7.39 (m, 2H), 7.22 (d, J = 7.6 Hz, 1H), 7.14 (dd, J = 2.0 Hz, 7.6 Hz, 1H), 7.04 (d, J = 8.4 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 143.8, 137.7, 133.3, 133.1, 132.8, 128.4, 127.5, 126.0, 116.6, 110.6, 100.0.



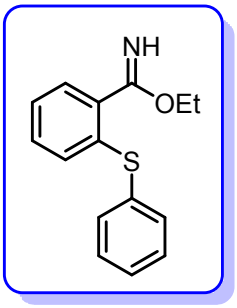
2-(Benzylthio)benzonitrile (3w),[6] **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.60 (dd, J = 1.2 Hz, 7.4 Hz, 1H), 7.43 (td, J = 1.6 Hz, 8.0 Hz, 1H), 7.35 (d, J = 7.6 Hz, 1H), 7.31-7.23 (m, 6H), 4.21 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 140.7, 135.9, 133.6, 132.7, 130.6, 128.8, 128.6, 127.5, 126.6, 117.1, 114.4, 38.7.



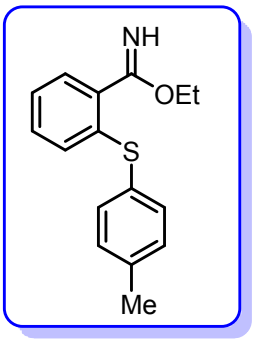
2-(Pentylthio)benzonitrile (3x), **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.60 (d, J = 7.6 Hz, 1H), 7.49 (t, J = 8.0 Hz, 1H), 7.40 (d, J = 8.0 Hz, 1H), 7.23 (t, J = 7.6 Hz, 1H), 3.01 (t, J = 7.2 Hz, 2H), 1.72-1.65 (m, 2H), 1.47-1.40 (m, 2H), 1.36-1.31 (m, 2H), 0.90 (t, J = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 142.2, 133.6, 132.7, 129.1, 128.6, 125.7, 117.2, 113.3, 33.5, 30.9, 28.4, 22.2, 13.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{12}H_{16}NS$: 206.0998, Found: 206.0996.



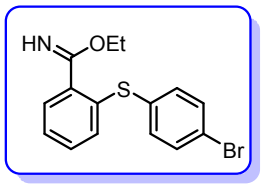
(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 4-cyano-3-(phenylthio)benzoate (3y), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.10 (s, 1H), 7.86 (dd, J = 1.2 Hz, 7.6 Hz, 1H), 7.70 (s, 1H), 7.53-7.49 (m, 2H), 7.44-7.42 (m, 3H), 4.80 (td, J = 4.4 Hz, 11.2 Hz, 22.0 Hz, 1H), 2.07-2.04 (m, 1H), 1.76-1.67 (m, 4H), 1.53-1.47 (m, 1H), 1.43-1.41 (m, 1H), 1.10-0.98 (m, 2H), 0.90 (d, J = 6.8 Hz, 3H), 0.85 (d, J = 7.2 Hz, 3H), 0.70 (d, J = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.1, 143.5, 134.9, 134.1, 133.6, 130.8, 130.0, 129.9, 129.4, 129.4, 126.9, 116.3, 115.8, 76.1, 47.0, 40.6, 34.1, 31.4, 26.5, 23.6, 22.0, 20.7, 16. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{28}NO_2$: 394.1835, Found: 394.1838.



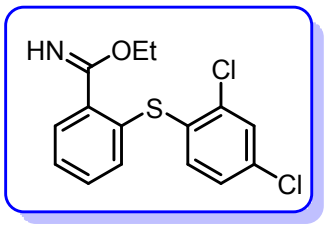
Ethyl 2-(phenylthio)benzimidate (4a), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.73 (d, J = 3.6 Hz, 2H), 7.51-7.48 (m, 4H), 7.35 (t, J = 8.0 Hz, 2H), 7.14 (t, J = 7.2 Hz, 1H), 4.45 (q, J = 6.8 Hz, 2H), 1.45 (t, J = 6.8 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.2, 137.4, 132.5, 130.4, 128.7, 128.3, 127.9, 127.5, 125.5, 125.0, 123.2, 62.5, 14.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{16}NOS$: 258.0947, Found: 258.0943.



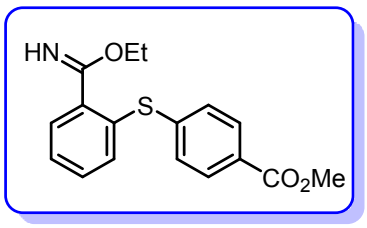
Ethyl 2-(*p*-tolylthio)benzimidate (4b), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79-7.73 (m, 2H), 7.47-7.37(m, 4H), 7.17 (d, J = 8.0 Hz, 2H), 4.43 (q, J = 6.4 Hz, 2H), 2.35 (s, 3H), 1.43 (t, J = 6.8 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 156.8, 139.8, 139.5, 135.4, 134.9, 132.5, 129.5, 129.46, 128.3, 127.9, 123.7, 62.4, 21.0, 14.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{18}NOS$: 272.1104, Found: 272.1101.



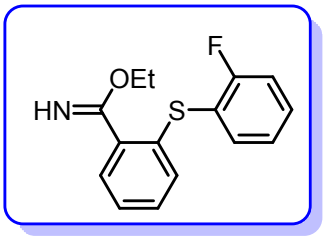
Ethyl 2-((4-bromophenyl)thio)benzimidate (4c), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.70 (d, J = 3.2 Hz, 2H), 7.48-7.42 (m, 5H), 7.35-7.32 (m, 1H), 4.43 (q, J = 6.8 Hz, 2H), 1.44 (t, J = 6.8 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.8, 139.9, 132.2, 131.7, 130.5, 129.4, 129.0, 128.6, 128.4, 127.8, 124.7, 62.6, 14.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{15}BrNOS$: 336.0052, Found: 336.0055.



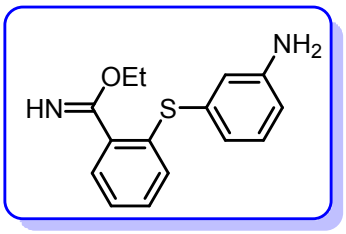
Ethyl 2-((2,4-dichlorophenyl)thio)benzimidate (4d), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.05 (d, J = 8.8 Hz, 1H), 7.77-7.75 (m, 1H), 7.59-7.57 (m, 1H), 7.35-7.31 (m, 4H), 4.59 (q, J = 6.8 Hz, 2H), 1.56 (t, J = 6.8 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.0, 157.4, 137.9, 134.8, 131.5, 129.9, 128.5, 128.3, 127.8, 127.3, 126.8, 63.8, 14.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{14}Cl_2NOS$: 326.0168, Found:
326.0163.



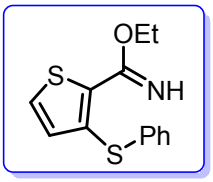
Methyl 4-((2-(ethoxy(imino)methyl)phenyl)thio)benzoate (4e), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.59 (d, J = 3.6 Hz, 1H), 8.12 (d, J = 7.6 Hz, 1H), 7.80 (d, J = 7.6 Hz, 2H), 7.56 (d, J = 7.2 Hz, 1H), 7.48-7.39 (m, 2H), 7.17 (dd, J = 6.8 Hz, 5.2 Hz, 1H), 4.45 (q, J = 7.2 Hz, 2H), 3.88 (s, 3H), 1.46 (t, J = 6.8 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.7, 157.8, 135.9, 134.3, 133.4, 132.6, 130.8, 129.0, 128.4, 127.3, 126.7, 125.8, 61.8, 52.3, 14.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{18}NO_3S$: 316.1002, Found: 316.1008.



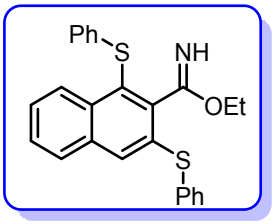
Ethyl 2-((2-fluorophenyl)thio)benzimidate (4f), **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.89 (t, J = 7.2 Hz, 1H), 7.79 (d, J = 3.6 Hz, 2H), 7.60-7.50 (m, 3H), 7.18 (t, J = 6.0 Hz, 1H), 7.06 (t, J = 8.8 Hz, 1H), 4.49 (q, J = 6.8 Hz, 2H), 1.50 (d, J = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 158.6, 156.9 (d, J = 236.0 Hz), 155.7, 132.2, 130.5, 130.3, 128.4, 128.2, 127.8, 126.9, 126.6, 126.0 (d, J = 7.0 Hz), 125.2 , 124.5 (d, J = 3.0 Hz), 62.6, 14.3. **^{19}F NMR (300 MHz, $CDCl_3$) δ** -111.17. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{15}H_{15}FNOS$: 276.0853, Found: 276.0851.



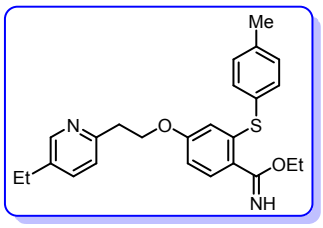
Ethyl 2-((3-aminophenyl)thio)benzimidate (4g), **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.24 (d, J = 3.6 Hz, 2H), 7.21-7.16 (m, 2H), 7.03 (t, J = 8.0 Hz, 1H), 6.96 (d, J = 8.0 Hz, 1H), 6.86 (s, 1H), 6.51 (d, J = 7.6 Hz, 1H), 4.37(q, J = 7.2 Hz, 2H), 1.41 (t, J = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 159.3, 149.3, 137.6, 131.3, 129.9, 129.3, 129.2, 128.0, 121.6, 120.7, 120.6, 62.5, 29.7, 14.3. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{15}H_{17}N_2OS$: 273.1056, Found: 273.1053.



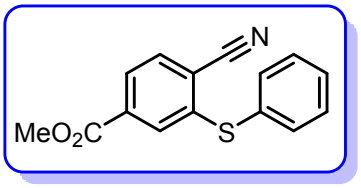
Ethyl 3-(phenylthio)thiophene-2-carbimidate (4h), **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.96 (d, J = 3.2 Hz, 1H), 7.54 (d, J = 7.6 Hz, 2H), 7.38 (t, J = 7.6 Hz, 2H), 7.20-7.16 (m, 2H), 4.42 (q, J = 7.2 Hz, 2H), 1.45 (t, J = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 149.8, 140.4, 133.5, 131.3, 129.1, 128.8, 127.5, 125.4, 123.3, 62.4, 14.3. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{13}H_{14}NOS_2$: 264.0511, Found: 264.0507.



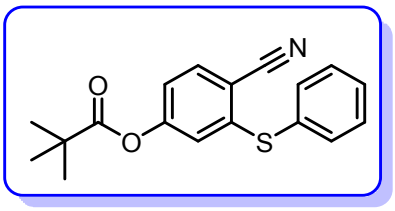
Ethyl 1,3-bis(phenylthio)-2-naphthimidate (4i), **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.27 (s, 1H), 7.95-7.93 (m, 5H), 7.90-7.49 (m, 6H), 7.37 (t, J = 7.6 Hz, 2H), 7.17-7.16 (m, 1H), 4.51 (q, J = 6.8 Hz, 2H), 1.49 (t, J = 6.8 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 157.2, 140.6, 133.9, 132.5, 129.8, 128.8, 128.7, 128.2, 127.7, 127.4, 126.6, 125.1, 124.5, 123.2, 62.6, 14.4. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{25}H_{22}NOS_2$: 416.1137, Found: 416.1140.



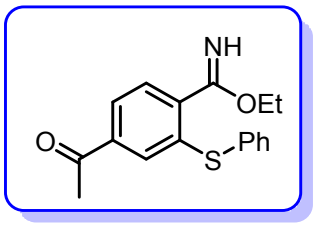
Ethyl 4-(2-(5-ethylpyridin-2-yl)ethoxy)-2-(*p*-tolylthio)benzimidate (4j), **^{1}H NMR (400 MHz, $CDCl_3$)** ***δ*** 8.35 (d, *J* = 1.6 Hz, 1H), 7.44-7.40 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.6 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 1H), 7.30 (dd, *J* = 2.4 Hz, 4.4 Hz, 1H), 6.57(s, 1H), 4.26 (q, *J* = 6.8 Hz, 2H), 4.19 (t, *J* = 6.8 Hz, 2H), 3.11 (t, *J* = 6.4 Hz, 2H), 2.61 (q, *J* = 7.6 Hz, 2H), 2.34 (s, 3H), 1.36 (t, *J* = 6.8 Hz, 3H), 1.23 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** ***δ*** 159.9, 155.2, 148.9, 138.3, 137.1, 135.8, 133.3, 131.5, 130.2, 129.9, 123.2, 116.2, 114.1, 112.2, 67.3, 37.2, 25.6, 21.1, 15.3, 14.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{29}N_2O_2S$: 421.1944, Found: 421.1941.



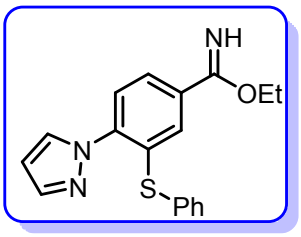
Methyl 4-cyano-3-(phenylthio)benzoate (3z),[6] **^{1}H NMR (400 MHz, $CDCl_3$)** ***δ*** 7.87 (dd, *J* = 1.2 Hz, 8.0 Hz, 1H), 7.77 (d, *J* = 1.2 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.50-7.48 (m, 2H), 7.50-7.48 (m, 3H), 3.87 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** ***δ*** 165.1, 143.2, 134.1, 133.7, 130.9, 130.5, 129.9, 129.3, 127.0, 116.4, 116.2, 52.7.



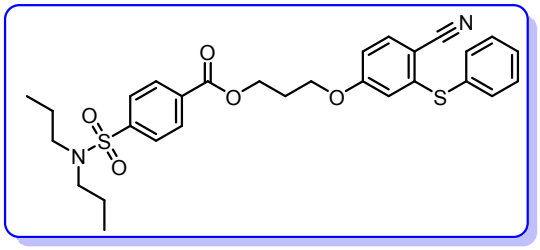
4-Cyano-3-(phenylthio)phenyl pivalate (3za), **^{1}H NMR (400 MHz, $CDCl_3$)** ***δ*** 7.64 (d, *J* = 8.4 Hz, 1H), 7.50-7.48 (m, 2H), 7.43-7.40 (m, 3H), 6.98 (dd, *J* = 2.0 Hz, 8.4 Hz, 1H), 6.81 (d, *J* = 2.0 Hz, 1H), 1.28 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** ***δ*** 176.0, 154.5, 144.3, 134.7, 133.6, 131.2, 129.8, 129.1, 122.9, 120.2, 116.5, 109.8, 39.2, 26.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{18}NO_2S$: 312.1053, Found:
312.1057.



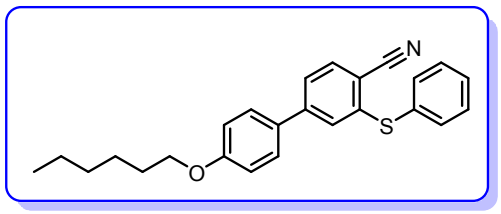
Ethyl 4-acetyl-2-(phenylthio)benzimidate (4k), **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.90 (dd, *J* = 8.0 Hz, 15.6 Hz, 1H), 7.78 (dd, *J* = 1.2 Hz, 8.0 Hz, 1H), 7.70 (s, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.40-7.38 (m, 2H), 7.36-7.33 (m, 2H), 4.29 (dd, *J* = 8.4 Hz, 15.2 Hz, 2H), 2.45 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 196.8, 138.2, 133.5, 132.6, 131.0, 129.6, 128.8, 128.4, 128.3, 127.1, 126.2, 62.2, 26.6, 14.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{18}NO_2S$: 312.1053, Found: 312.1057.



Ethyl 3-(phenylthio)-4-(1*H*-pyrazol-1-yl)benzimidate (4l), **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.89 (dd, *J* = 2.4 Hz, 16.8 Hz, 2H), 7.76 (d, *J* = 1.6 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.35-7.31 (m, 6H), 6.46 (t, *J* = 2.0 Hz, 1H), 4.31 (dd, *J* = 7.2 Hz, 14.4 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 1165.3, 142.7, 141.2, 132.9, 132.5, 130.9, 130.2, 129.6, 128.3, 126.1, 107.2, 61.3, 14.2. HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{18}H_{18}N_3OS$: 324.1165, Found: 324.1167.

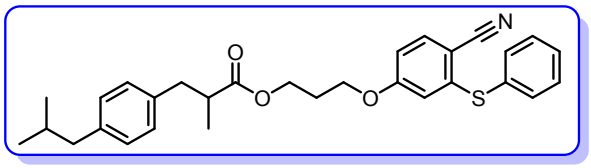


3-(4-Cyano-3-(phenylthio)phenoxy)propyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (3zb), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15-8.10 (m, 2H), 7.88-7.86 (m, 2H), 7.59-7.54 (m, 1H), 7.49-7.46 (m, 2H), 7.41-7.39 (m, 2H), 6.95 (d, *J* = 8.8 Hz, 1H), 6.75 (dd, *J* = 2.4 Hz, 8.4 hz, 1H), 6.58 (d, *J* = 5.6 Hz, 1H), 4.48 (t, *J* = 6.0 Hz, 2H), 4.02 (d, *J* = 6.0 Hz, 2H), 3.10 (t, *J* = 7.6 Hz, 4H), 2.24-2.18 (m, 2H), 1.55 (dd, *J* = 7.2 Hz, 6.8 Hz, 4H), 0.87 (t, *J* = 7.2 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 165.1, 161.9, 144.5, 144.3, 135.2, 134.0, 133.6, 133.2, 130.1, 129.7, 129.0, 127.0, 119.0, 117.1, 115.7, 115.1, 112.7, 104.8, 64.7, 62.1, 49.9, 28.3, 21.9, 11.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{33}N_2O_5S_2$: 553.1825, Found: 553.1829.

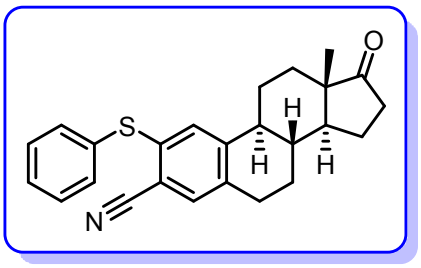


4'-(Hexyloxy)-3-(phenylthio)-[1,1'-biphenyl]-4-carbonitrile (3zc), **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.67 (d, *J* = 8.0 Hz, 1H), 7.54-7.48 (m, 2H), 7.44 (dd, *J* = 1.6 Hz, 8.0 Hz, 1H), 7.41-7.34 (m, 6H), 6.94-6.91 (m, 2H), 3.97 (t, *J* = 6.4 Hz, 2H), 1.82-1.75 (m, 2H), 1.48-1.42 (m, 2H), 1.35-1.32 (m, 4H), 0.93-

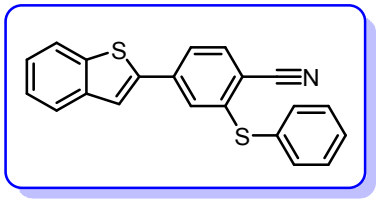
0.89 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 159.9, 145.6, 142.0, 134.0, 133.6, 133.0, 132.3, 130.7, 128.7, 128.4, 128.2, 124.9, 117.2, 115.0, 111.1, 68.1, 31.5, 29.1, 25.6, 22.6, 14.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{26}NOS$: 388.1730, Found: 388.1736.



3-(4-Cyano-3-(phenylthio)phenoxy)propyl 3-(4-isobutylphenyl)-2-methylpropanoate (3zd), **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.53-7.46 (m, 3H), 7.42-7.38 (m, 3H), 7.18 (d, J = 8.0 Hz, 2H), 7.12 (dd, J = 8.0 Hz, 3H), 7.05-7.02 (m, 1H), 4.20-4.14 (m, 1H), 3.76 (t, J = 6.4 Hz, 2H), 3.49 (q, J = 7.2 Hz, 1H), 2.43 (q, J = 7.2 Hz, 2H), 1.97 (t, J = 6.4 Hz, 1H), 1.87-1.83 (m, 1H), 1.49 (d, J = 7.2 Hz, 3H), 1.46 (d, J = 7.2 Hz, 2H), 1.34-1.27 (m, 2H), 0.88 (t, J = 7.2 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 173.5, 162.0, 146.0, 144.1, 140.5, 144.1, 140.5, 137.6, 133.6, 129.5, 129.2, 127.2, 127.0, 115.9, 112.6, 112.5, 64.5, 60.8, 47.9, 46.8, 45.0, 32.8, 32.7, 30.1, 25.4, 22.3, 18.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{34}NO_3S$: 488.2254, Found: 488.2258.

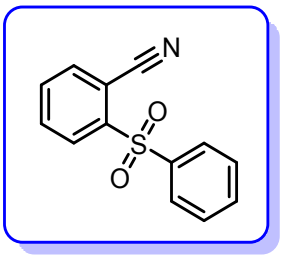


(8*R*,9*S*,13*S*,14*S*)-13-Methyl-17-*oxo*-2-(phenylthio)-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthrene-3-carbonitrile (3ze), **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.81-7.78 (m, 1H), 7.41-7.32 (m, 3H), 7.29 (d, J = 8.0 Hz, 1H), 7.23-7.20 (m, 1H), 7.13 (t, J = 7.2 Hz, 1H), 4.39-4.32 (m, 2H), 2.99-2.94 (m, 2H), 2.55-2.43 (m, 2H), 2.31-2.20 (m, 1H), 2.18-2.13 (m, 1H), 2.06-2.00 (m, 2H), 1.55-1.49 (m, 2H), 1.38 (t, J = 7.2 Hz, 2H), 1.28-1.26 (m, 1H), 0.92 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 166.7, 159.5, 145.0, 142.6, 137.2, 136.6, 130.1, 128.8, 128.4, 126.8, 125.3, 123.5, 50.4, 47.9, 44.7, 37.8, 35.8, 31.5, 29.0, 26.3, 25.6, 21.6, 13.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{26}NOS$: 388.1730, Found: 388.1733.

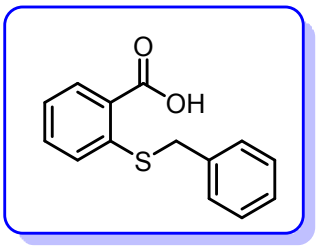


4-(Benzo[*b*]thiophen-2-yl)-2-(phenylthio)benzonitrile (5), **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.67 (d, J = 8.0 Hz, 1H), 7.58-7.53 (m, 4H), 7.47-7.43 (m, 5H), 7.37-7.34 (m, 2H), 7.11 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 145.1, 143.1, 141.2, 140.1, 139.9, 138.9, 134.1, 133.6, 129.9, 129.4, 129.1, 127.3, 125.4, 124.9,

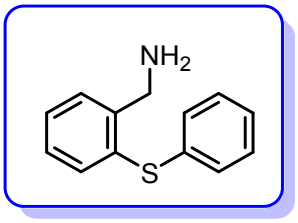
124.2, 123.9, 122.3, 122.0, 116.8. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{21}H_{14}NS_2$: 344.0562, Found: 344.0567.



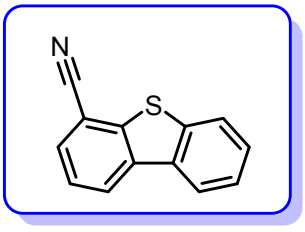
2-(Phenylsulfonyl)benzonitrile (6), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.36-8.34 (m, 1H), 8.10-8.08 (m, 2H), 7.82-7.78 (m, 2H), 7.71-7.63 (m, 2H), 7.58-7.54 (m, 2H). **^{13}C NMR (100 MHz, d6-DMSO)** δ 143.7, 139.5, 135.6, 134.2, 133.3, 133.2, 129.8, 129.4, 128.7, 128.5, 126.9, 115.6, 111.4. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{13}H_{10}NO_2S$: 244.0427, Found: 244.0423.



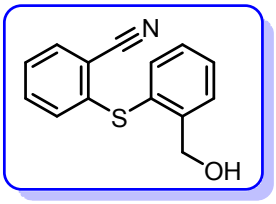
2-(Benzylthio)benzoic acid (**7**), **^{1}H NMR (400 MHz, *d*6-DMSO)** δ 8.02 (d, J = 7.6 Hz, 1H), 7.61-7.60 (m, 2H), 7.55 (d, J = 7.2 Hz, 2H), 7.45 (t, J = 7.2 Hz, 2H), 7.38 (t, J = 7.2 Hz, 1H), 7.36-7.30 (m, 1H), 4.32 (s, 2H). **^{13}C NMR (100 MHz, d6-DMSO)** δ 172.7, 146.5, 141.8, 137.6, 136.2, 134.4, 133.7, 132.9, 132.4, 130.9, 129.2, 40.9. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{14}H_{13}O_2S$: 245.0631, Found: 245.0634.



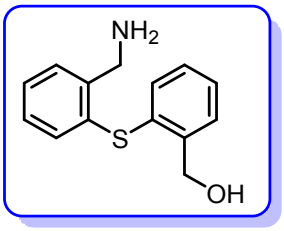
(2-(Phenylthio)phenyl)methanamine (8), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 (d, J = 7.2 Hz, 1H), 7.33 (t, J = 6.8 Hz, 2H), 7.30-7.23 (m, 3H), 7.21-7.20 (m, 3H), 3.95 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 144.6, 136.2, 133.9, 132.9, 129.6, 129.2, 128.7, 128.5, 127.9, 126.5, 45.0. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C13H14NS: 216.0841, Found: 216.0845.



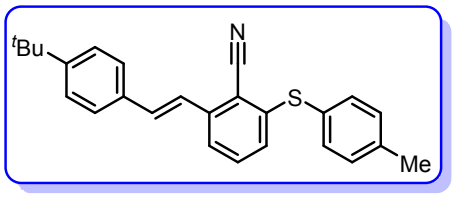
Dibenzo[b,d]thiophene-4-carbonitrile (9),[8] **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.30 (d, J = 8.0 Hz, 1H), 8.14 (dd, J = 1.6 Hz, 6.0 Hz, 1H), 7.90-7.88 (m, 1H), 7.75 (d, J = 0.8 Hz, 7.6 Hz, 1H), 7.56-7.49 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 412.8, 138.9, 136.5, 134.5, 130.9, 127.9, 125.5, 125.1, 124.5, 123.0, 121.9, 117.1, 106.8.



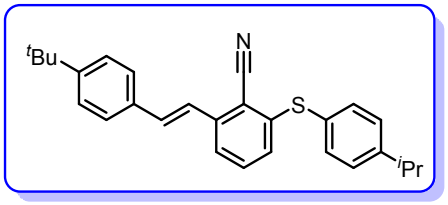
2-((2-(Hydroxymethyl)phenyl)thio)benzonitrile (3zf), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.61 (d, J = 7.6 Hz, 2H), 7.46-7.36 (m, 3H), 7.33-7.29 (m, 1H), 7.25-7.22 (m, 1H), 6.96 (d, J = 8.0 Hz, 1H), 4.80 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.9, 142.0, 135.3, 133.7, 133.1, 129.9, 129.0, 128.7, 128.7, 126.3, 116.8, 112.3, 63.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{14}NOS$: 216.0841, Found: 216.0845.



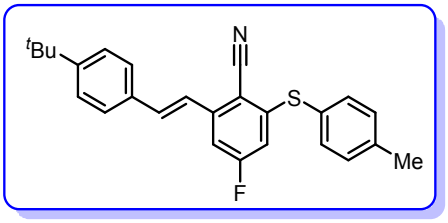
(2-((2-(Aminomethyl)phenyl)thio)phenyl)methanol (10), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.41 (d, J = 7.2 Hz, 1H), 7.21 (d, J = 7.2 Hz, 1H), 7.18-7.11 (m, 2H), 7.08-7.00 (m, 4H), 4.61 (s, 2H), 3.77 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 142.7, 141.8, 133.5, 132.7, 132.1, 131.8, 128.7, 128.2, 128.0, 127.9, 127.7, 127.6, 62.3, 44.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{16}NOS$: 246.0947, Found: 246.0943.



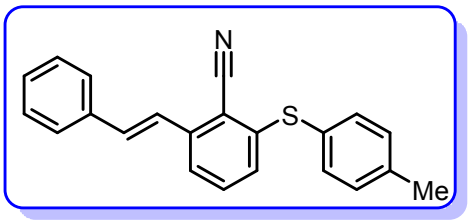
(*E*)-2-(4-(*tert*-Butyl)styryl)-6-(*p*-tolylthio)benzonitrile (12a), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55-7.51 (m, 3H), 7.43-7.40 (m, 5H), 7.34-7.30 (m, 1H), 7.25-7.22 (m, 3H), 6.88 (d, J = 7.6 Hz, 1H), 2.40 (s, 3H), 1.35 (s, 9H), **^{13}C NMR (100 MHz, $CDCl_3$)** δ 152.2, 144.2, 142.2, 139.4, 134.3, 133.7, 133.4, 132.3, 130.6, 126.9, 125.8, 123.3, 122.0, 34.7 31.2, 21.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{26}NS$: 384.1780, Found: 384.1783.



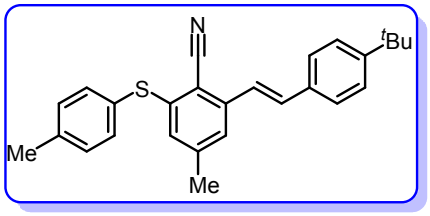
(*E*)-2-(4-(*tert*-Butyl)styryl)-6-((4-isopropylphenyl)thio)benzonitrile (12b), **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.78 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.58-7.53 (m, 1H), 7.54-7.51 (m, 3H), 7.46-7.44 (m, 1H), 7.42-7.40 (m, 3H), 7.33-7.28 (m, 2H), 7.26-7.20 (m, 1H), 2.68 (q, J = 7.6 Hz, 1H), 1.36 (d, J = 2.4 Hz, 3H), 1.35 (s, 9H), 1.27 (d, J = 7.2 Hz, 3H), **^{13}C NMR (100 MHz, $CDCl_3$) δ** 152.2, 145.7, 144.2, 142.2, 140.8, 134.3, 133.7, 133.4, 133.3, 133.1, 132.7, 132.3, 129.4, 127.3, 126.9, 125.8, 125.2, 123.3, 122.1, 118.0, 115.9, 111.1, 34.7, 31.2, 28.6, 15.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{28}H_{30}NS$: 412.2093, Found: 412.2095.



(*E*)-2-(4-(*tert*-Butyl)styryl)-4-fluoro-6-(*p*-tolylthio)benzonitrile (12c), **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.55-7.51 (m, 2H), 7.47-7.42 (m, 4H), 7.38-7.36 (m, 1H), 7.27 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 16.0 Hz, 1H), 7.16 (dd, J = 2.4 Hz, 9.6 Hz, 1H), 6.41 (dd, J = 2.4 Hz, 8.8 Hz, 1H), 2.42 (s, 3H), 1.34 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 164.9 (d, J = 254.0 Hz), 152.7, 148.7, 144.8, 140.5, 135.2, 134.9, 132.9, 130.9, 129.7, 128.6, 127.1, 125.8, 122.3, 115.3, 113.2, 112.9, 108.7, 108.5, 34.8, 31.2, 21.3. **^{19}F NMR (300 MHz, $CDCl_3$) δ** -103.57, HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{25}FNS$: 402.1686, Found: 402.1689.

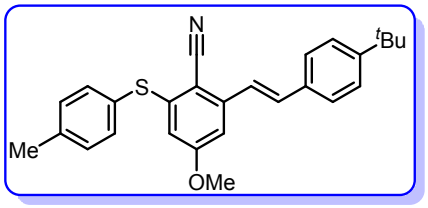


(*E*)-2-Styryl-6-(*p*-tolylthio)benzonitrile (12d), **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.58-7.53 (m, 2H), 7.45-7.28 (m, 5H), 7.34-7.33 (m, 2H), 7.23-7.21 (m, 4H), 6.99 (d, J = 8.0 Hz, 1H), 2.39 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 134.3, 133.9, 132.3, 130.5, 128.8, 127.1, 124.0, 122.0, 113.5, 21.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{18}NS$: 328.1154, Found: 328.1151.

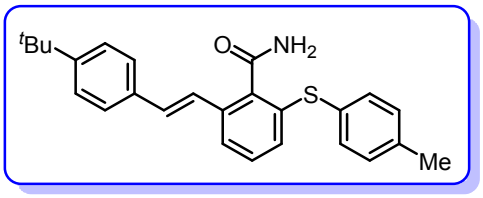


(*E*)-2-(4-(*tert*-Butyl)styryl)-4-methyl-6-(*p*-tolylthio)benzonitrile (12e), **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.53-7.50 (m, 2H), 7.43-7.38 (m, 6H), 7.24-7.20 (m, 3H), 6.76 (d, J = 2.0 Hz, 1H), 2.39 (d, J = 3.2 Hz, 3H), 2.30 (d, J = 3.2 Hz, 3H), 1.35 (d, J = 3.6 Hz, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** 143.2, 133.9, 133.4,

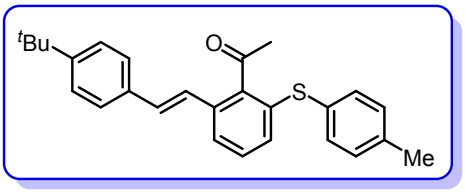
130.5, 128.4, 126.9, 125.7, 123.4, 123.2, 108.5, 105.4, 34.7, 31.2 21.9, 21.3. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{27}H_{28}NS$: 398.1937, Found: 398.1941.



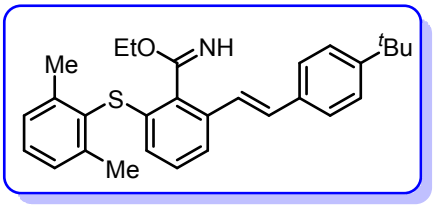
(*E*)-2-(4-(*tert*-Butyl)styryl)-4-methoxy-6-(*p*-tolylthio)benzonitrile (12f), **^{1}H NMR (400 MHz, $CDCl_3$)** ***δ*** 7.51 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 11.6 Hz, 4H), 7.38 (d, *J* = 6.8 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 3H), 6.99 (dd, *J* = 1.2 Hz, 1H), 6.39 (dd, *J* = 1.6 Hz, 1H), 3.75 (s, 3H), 2.38 (s, 3H), 1.34 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** ***δ*** 162.4, 152.3, 146.1, 143.8, 139.3, 134.5, 133.6, 130.5, 126.9, 125.8, 123.4, 113.4, 107.1, 55.5, 31.2, 29.7 21.3. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{27}H_{28}NOS$: 414.1886, Found: 414.1883.



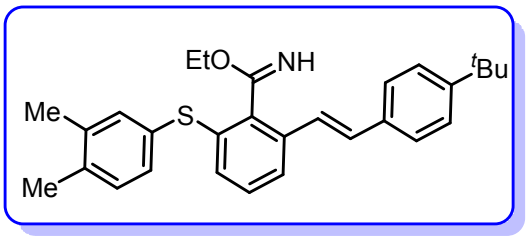
(*E*)-2-(4-(*tert*-Butyl)styryl)-6-(*p*-tolylthio)benzamide (12a-1), **^{1}H NMR (400 MHz, $CDCl_3$)** ***δ*** 7.71 (d, *J* = 7.6 Hz, 1H), 7.53-7.50 (m, 2H), 7.45-7.42 (m, 2H), 7.40-7.38 (m, 2H), 7.37-7.32 (m, 3H), 7.10 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 16.4 Hz, 1H), 2.32 (s, 3H), 1.33 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** ***δ*** 169.1, 149.2, 137.3, 136.6, 133.6, 131.7, 130.5, 129.9, 129.7, 129.7, 128.1, 127.6, 126.9, 125.9, 125.6, 125.3, 119.2, 35.7, 31.3. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{26}H_{27}NOS$: 401.1881, Found: 401.1883.



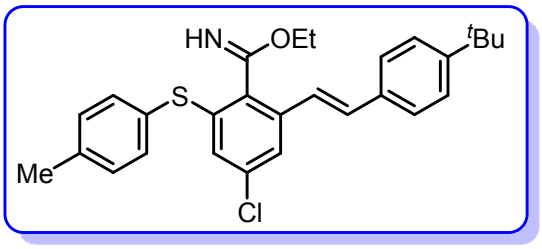
(*E*)-1-(2-(4-(*tert*-Butyl)styryl)-6-(*p*-tolylthio)phenyl)ethan-1-one (12a-2), **^{1}H NMR (400 MHz, $CDCl_3$)** ***δ*** 7.54 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.41-7.39 (m, 1H), 7.40-7.38 (m, 3H), 7.36-7.35 (m, 1H), 7.29-7.27 (m, 1H), 7.26-7.24 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 2.54 (s, 3H), 2.32 (s, 3H), 1.32 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** ***δ*** 205.7, 151.6, 137.4, 133.9, 132.4, 131.6, 131.4, 131.0, 130.1, 129.4, 126.6, 126.3, 125.7, 125.2, 124.8, 123.5, 34.7, 32.7, 31.2, 21.1. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{27}H_{28}OS$: 400.0981, Found: 400.0983.



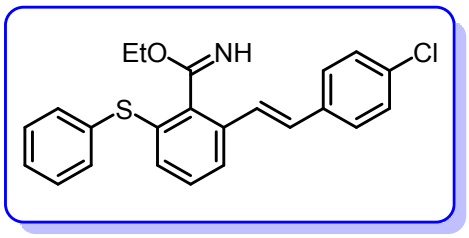
Ethyl (*E*)-2-(4-(*tert*-butyl)styryl)-6-((2,6-dimethylphenyl)thio)benzimidate (14a), **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.43-7.37 (m, 6H), 7.24-7.22 (m, 1H), 7.17 (d, J = 7.6 Hz, 2H), 7.08 (d, J = 6.8 Hz, 2H), 6.42 (d, J = 7.6 Hz, 1H), 4.48 (dd, J = 6.8 Hz, 14.0 Hz, 2H), 2.41 (s, 6H), 1.47 (t, J = 7.2 Hz, 3H), 1.34 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 151.3, 143.9, 136.3, 135.4, 134.3, 133.5, 131.2, 130.6, 129.3, 129.3, 128.5, 126.5, 125.6, 124.5, 121.6, 62.1, 34.6, 31.3, 21.8, 14.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{34}NOS$: 444.2356, Found: 444.2358.



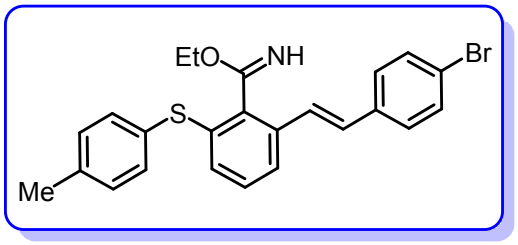
Ethyl (*E*)-2-(4-(*tert*-butyl)styryl)-6-((3,4-dimethylphenyl)thio)benzimidate (14b), **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.53 (d, J = 7.6 Hz, 1H), 7.45-7.34 (m, 5H), 7.23-7.19 (m, 2H), 7.16-7.12 (m, 1H), 7.01-7.07 (m, 2H), 7.02 (d, J = 8.0 Hz, 1H), 4.41 (q, J = 7.2 Hz, 2H), 2.25 (s, 3H), 2.23 (s, 3H), 1.40 (t, J = 7.2 Hz, 3H), 1.33 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 151.3, 137.8, 136.7, 135.9, 135.5, 134.3, 133.8, 131.2, 130.5, 130.3, 129.7, 129.3, 126.5, 125.6, 124.5, 123.2, 62.1, 34.6, 31.2, 19.6, 19.4, 14.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{34}NOS$: 444.2356, Found: 444.2358.



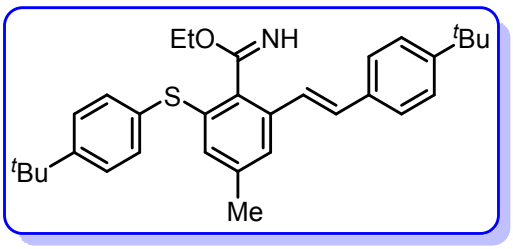
Ethyl (*E*)-2-(4-(*tert*-butyl)styryl)-4-chloro-6-(*p*-tolylthio)benzimidate (14c), **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.47 (d, J = 1.6 Hz, 1H), 7.40 (d, J = 2.0 Hz, 3H), 7.34 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 7.03 (dd, J = 16.4 Hz, 24.8 Hz, 3H), 6.88 (d, J = 2.0 Hz, 1H), 4.40 (dd, J = 6.8 Hz, 14.0 Hz, 2H), 2.37 (s, 3H), 1.40 (t, J = 7.2 Hz, 3H), 1.33 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 151.7, 138.8, 138.1, 137.1, 135.4, 133.5, 132.4, 130.4, 129.2, 128.7, 127.8, 126.6, 125.7, 123.2, 122.8, 62.2, 34.7, 31.2, 21.2, 14.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{28}H_{31}ClNOS$: 464.1809, Found: 464.1805.



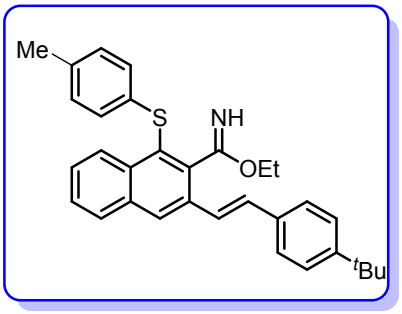
Ethyl (*E*)-2-(4-chlorostyryl)-6-(phenylthio)benzimidate (14d), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.68-7.66 (m, 2H), 7.48-7.41 (m, 2H), 7.37-7.35 (m, 3H), 7.32-7.28 (m, 4H), 7.16-7.07 (m, 1H), 7.16-7.07 (m, 1H), 6.99-6.05 (m, 1H), 4.58-4.53 (m, 2H), 2.32 (s, 3H), 1.45-1.42 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.7, 135.6, 134.4, 133.5, 130.3, 129.5, 128.8, 127.9, 125.6, 124.7, 124.3, 62.8, 20.9, 14.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{21}ClNOS$: 394.1027, Found: 394.1029.



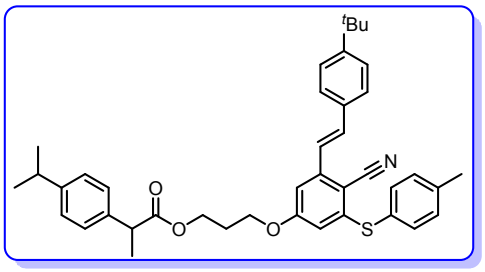
Ethyl (*E*)-2-(4-bromostyryl)-6-(*p*-tolylthio)benzimidate (14e), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 (d, J = 8.0 Hz, 2H), 7.46-7.43 (m, 5H), 7.32-7.28 (m, 4H), 7.07 (d, J = 8.0 Hz, 1H), 6.98 (d, J = 8.0 Hz, 1H), 4.54 (dd, J = 7.2 Hz, J = 14.0 Hz, 2H), 1.43 (t, J = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** 158.6, 136.0, 134.4, 131.8, 130.3, 129.8, 129.4, 128.2, 125.7, 124.7, 124.3, 121.7, 62.8, 20.9, 14.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{23}BrNOS$: 452.0678, Found: 452.0681.



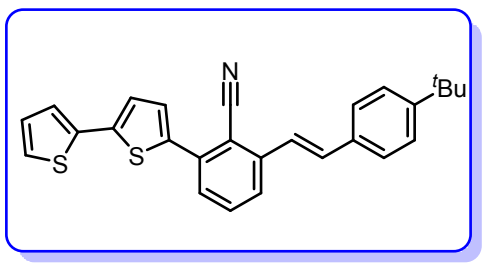
Ethyl (*E*)-2-((4-(*tert*-butyl)phenyl)thio)-6-(4-(*tert*-butyl)styryl)-4-methylbenzimidate (14f), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46-7.43 (m, 2H), 7.40-7.32 (m, 6H), 7.32-7.28 (d, J = 8.0 Hz, 1H), 7.28(d, J = 2.4 Hz, 1H), 7.12 (d, J = 13.6 Hz, 1H), 7.08(s, 1H), 6.93 (d, J = 8.0 Hz, 1H), 4.47-4.43(m, 2H), 2.32 (s, 3H), 1.35-1.34(m, 3H), 1.31-1.28(m, 18H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.8, 1315, 131,5, 130.5, 126.6, 126.0, 125.6, 123.9, 95.2, 62.9, 34.6, 31.3, 21.5, 14.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{32}H_{40}NOS$: 486.2825, Found: 486.2822.



Ethyl (*E*)-3-(4-(*tert*-butyl)styryl)-1-(*p*-tolylthio)-2-naphthimidate (14g), **^{1}H NMR (400 MHz, $CDCl_3$)** ***δ*** 8.18 (d, *J* = 13.2 Hz, 1H), 7.89-7.85 (m, 3H), 7.53-7.48 (m, 4H), 7.42-7.38 (m, 2H), 7.32(d, *J* = 8.4 Hz, 2H), 7.21-7.17(m, 1H), 7.12 (d, *J* = 8.4 Hz, 2H), 4.54 (dd, *J* = 14.4 Hz, 7.2 Hz, 2H), 2.32(s, 3H), 1.46 (t, *J* = 7.2 Hz, 3H), 1.33 (d, *J* = 6.8 Hz, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** ***δ*** 159.4, 151.0, 141.8, 134.9, 134.0, 132.1, 131.7, 131.1, 129.6, 129.4, 128.1, 127.9, 127.4, 126.5, 125.6, 124.9, 124.8, 124.1, 62.7, 31.2, 29.6, 20.9, 14.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{32}H_{34}NOS$: 480.2356, Found: 480.2356.

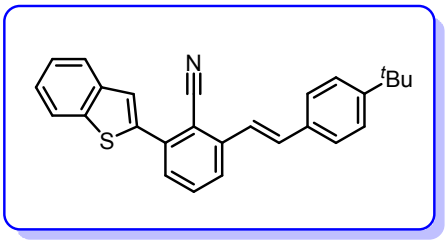


(*E*)-3-(3-(4-(*tert*-Butyl)styryl)-4-cyano-5-(*p*-tolylthio)phenoxy)propyl 2-(4-isopropylphenyl) propanoate (12g), **^{1}H NMR (400 MHz, $CDCl_3$)** ***δ*** 8.13 (d, *J* = 8.4 Hz, 1H), 7.47-7.42 (m, 4H), 7.22 (d, *J* = 4.8 Hz, 2H), 7.20-7.13 (m, 6H), 7.01 (d, *J* = 7.6 Hz, 2H), 6.81-6.79 (m, 1H), 4.68 (q, *J* = 7.2 Hz, 2H), 4.32-4.28 (m, 2H), 3.98 (t, *J* = 6.0 Hz, 1H), 3.70 (dd, *J* = 10.4 Hz, 7.2 Hz, 1H), 2.37(s,3H), 2.10-2.04(m, 2H), 1.48 (d, *J* = 7.2 Hz, 3H), 1.35(s,9H), 0.84 (d, *J* = 6.8Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** 174.7, 160.6, 151.1, 142.0, 140.5, 137.7), 136.4, 133.4, 130.8, 130.2, 129.3, 127.6, 127.1, 125.4, 121.1, 118.8, 114.6, 104.8, 64.8, 64.5, 61.2, 45.1, 44.9, 34.7), 31.2, 30.1, 29.6, 28.5, 22.3, 21.6, 21.4, 18.3, 14.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{41}H_{46}NO_3S$: 632.3193, Found: 632.3197.



(*E*)-2-([2,2'-Bithiophen]-5-yl)-6-(4-(*tert*-butyl)styryl)benzonitrile (15a), **^{1}H NMR (400 MHz, $CDCl_3$)** ***δ*** 7.76 (d, *J* = 8.0 Hz, 1H), 7.64-7.55 (m, 2H), 755-7.49 (m, 4H), 7.44-7.38 (m, 4H), 7.29-7.24 (m, 2H), 7.23-7.20 (m, 1H), 1.33 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** 152.0, 140.7, 133.4, 133.3, 133.2, 133.1,

130.0, 132.6, 127.2, 126.8, 125.7, 125.0, 123.2, 118.0, 111.0, 34.7, 31.2. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{27}H_{24}NS_2$: 426.1345, Found: 426.1348.



(*E*)-2-(Benzo[*b*]thiophen-2-yl)-6-(4-(*tert*-butyl)styryl)benzonitrile (15b), ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.78 (d, J = 8.0 Hz, 1H), 7.64 (t, J = 8.0 Hz, 2H), 7.55-7.50 (m, 4H), 7.46 (s, 1H), 7.43-7.39 (m, 3H), 7.29-7.26 (m, 2H), 7.24-7.23 (m, 1H), 1.34 (s, 9H). **^{13}C NMR (100 MHz, CDCl$_3$)** 152.1, 152.0, 141.4, 140.7, 133.2, 133.1, 132.7, 127.3, 126.9, 125.7, 125.1, 123.2, 118.0, 111.1, 34.7, 31.2. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{27}H_{24}NS$: 394.1624, Found: 394.1626.

F. References:

1) M. A. Fernndez-Rodrguez, Q. Shen, J. F. Hartwig, *Chem. Eur. J*., 2006, **12**, 7782-7796.

2) X. Wei, Y. Chen, R. Duan, J. Liu, R. Wang, Y. Liu, Z. Li, Y. Yi, Y. Yamada-Takamura, P. Wangac, Y. Wang, *J. Mater. Chem. C*. 2017, **5**, 12077-12084.

3) J. Ann, A. Jung, M.-Y. Kim, H.-M. Kim, H. C. Ryu, S. Kim, D. W. Kang, S. Hong, M. Cui, S. Choi, P. M. Blumberg, R. Frank-Foltyn, G. Bahrenberg, H. Stockhausen, T. Christoph, J. Lee, *Bioorg. Med. Chem*., 2015, **23**, 6844-6854.

4) M. Pawliczek, L. B. Garve, D. Werz, *Org. Lett*., 2015, **17**, 1716-719.

5) M. Arisawa, T. Suzuki, T. Ishikawa, M. Yamaguchi, *J. Am. Chem. Soc*., 2008, **130**, 12214-12215.

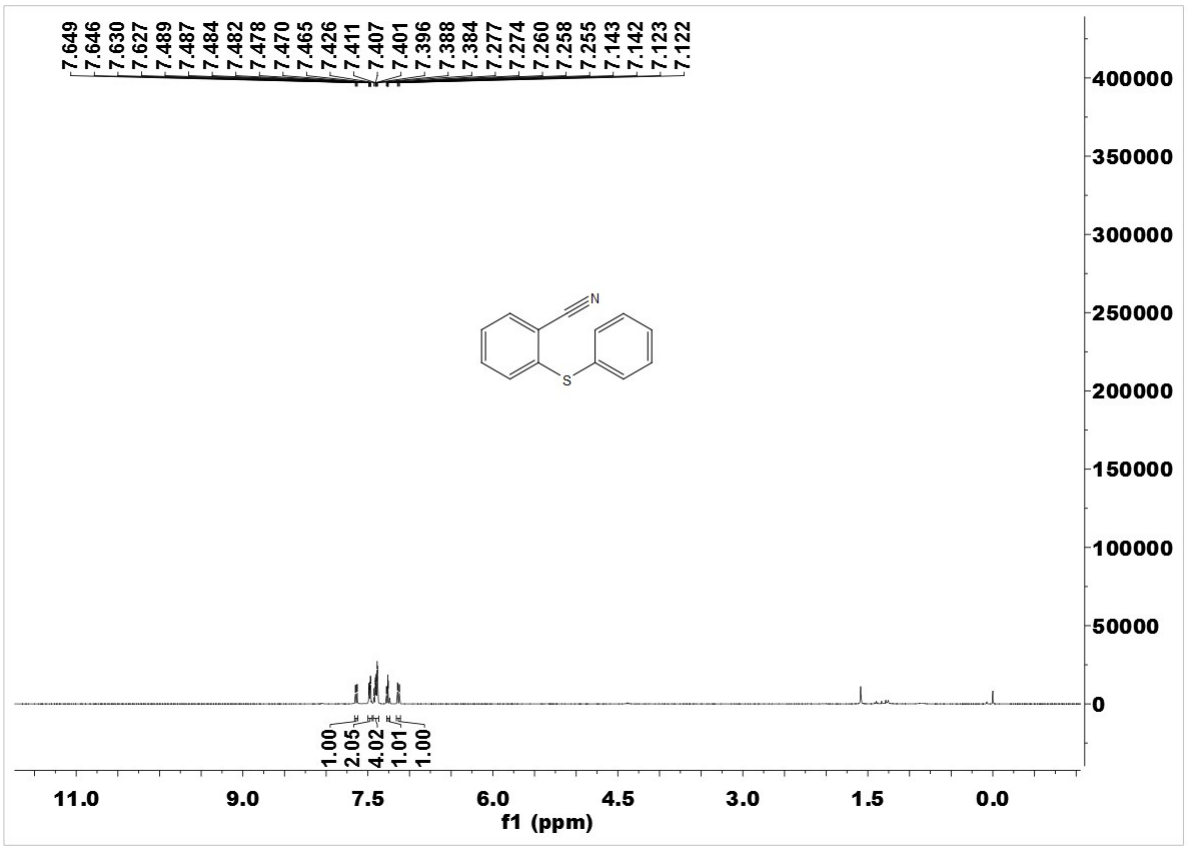
6) Y. Zhou, Y. Wang, Y. Lou, Q. Song, *Chem. Commun*., 2019, **55**, 10265-10268.

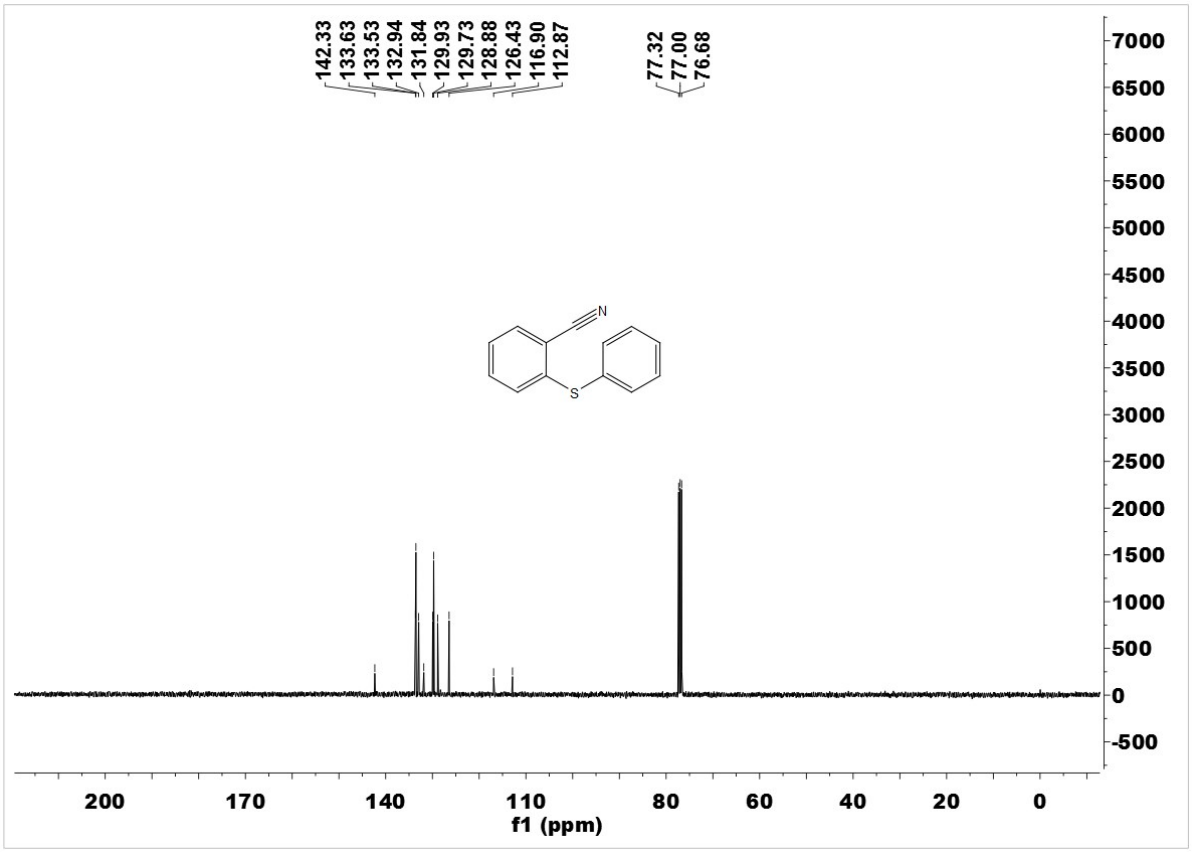
7) M. Pawliczek, L. B. Garve, D. Werz, *Org. Lett*. 2015, **17**, 1716-719.

8) L.-Y. Liu, K.-S. Yeung, J.-Q. Yu, *Chem. Eur. J*., 2019, **25**, 2199-2202.

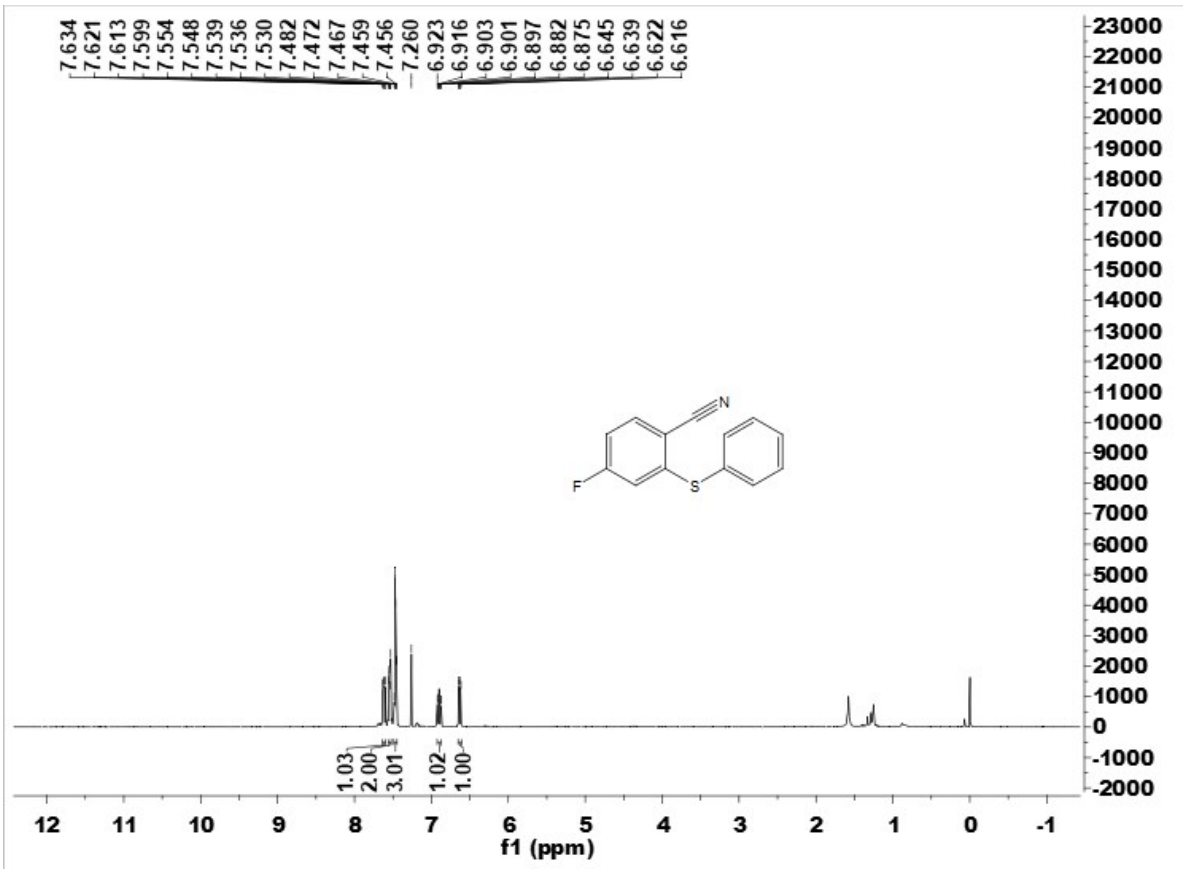
G. NMR Spectrum

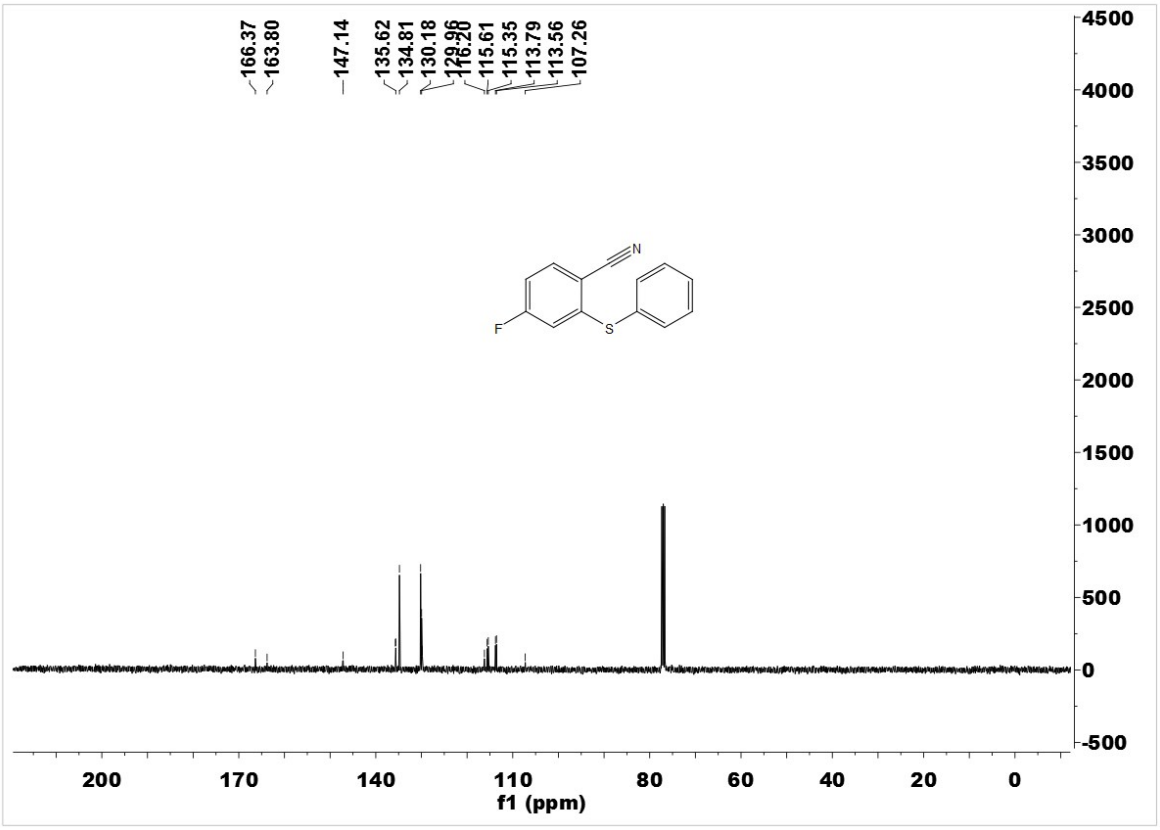
2-(Phenylthio)benzonitrile (3a)

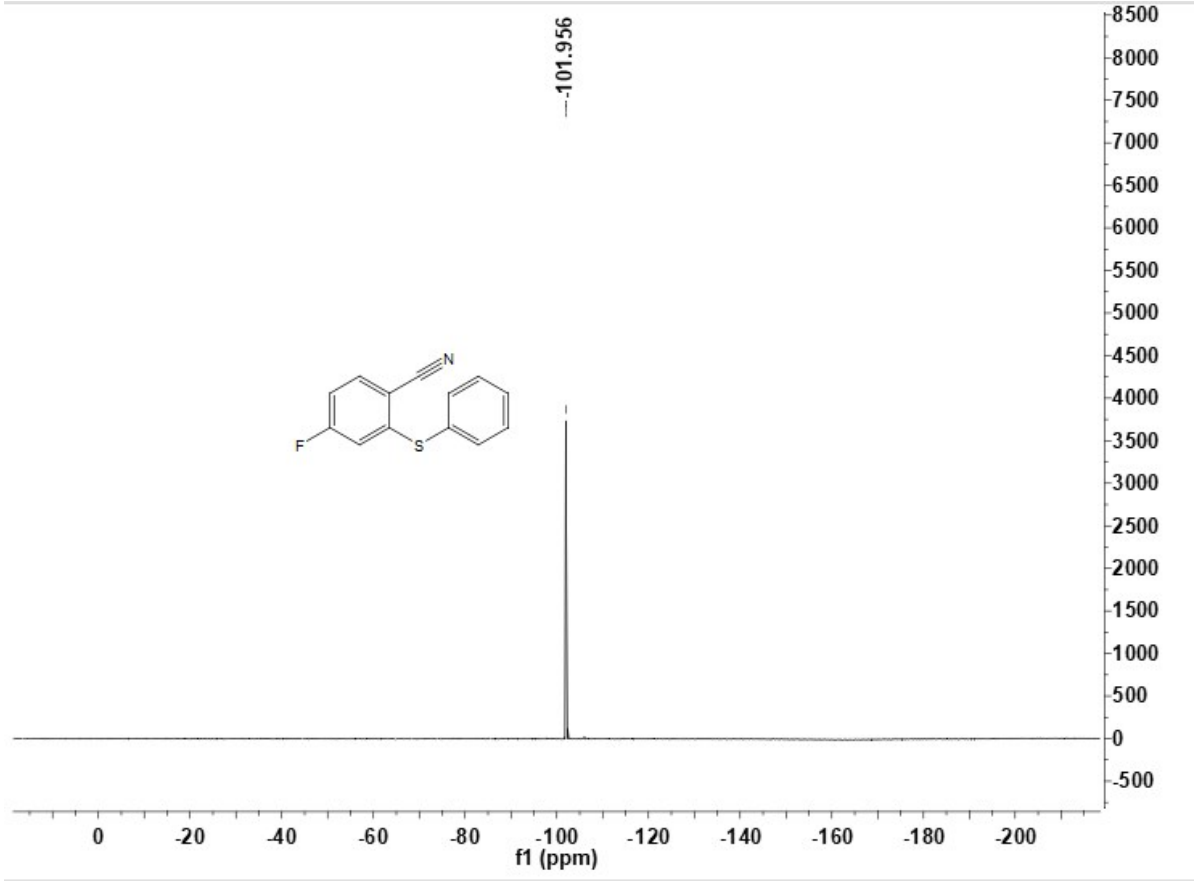




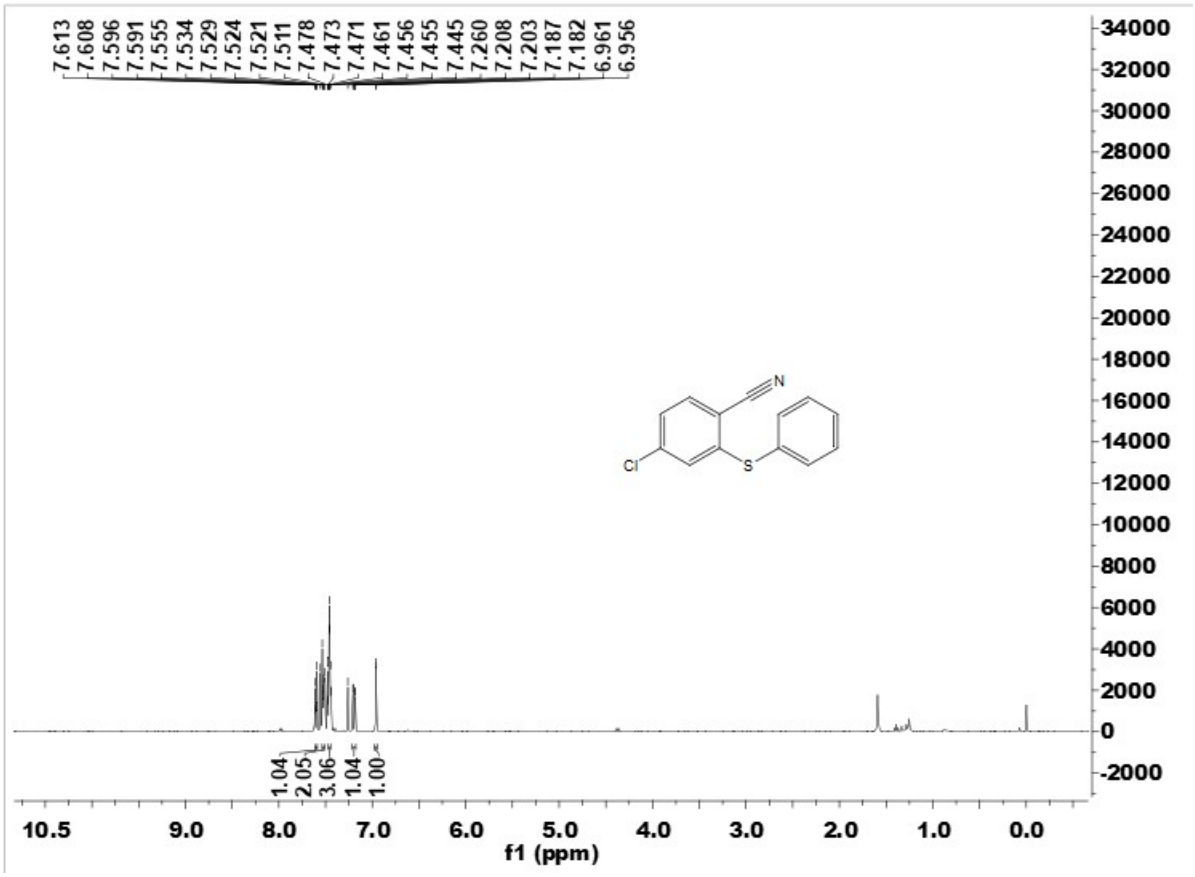
4-Fluoro-2-(phenylthio)benzonitrile (3b)

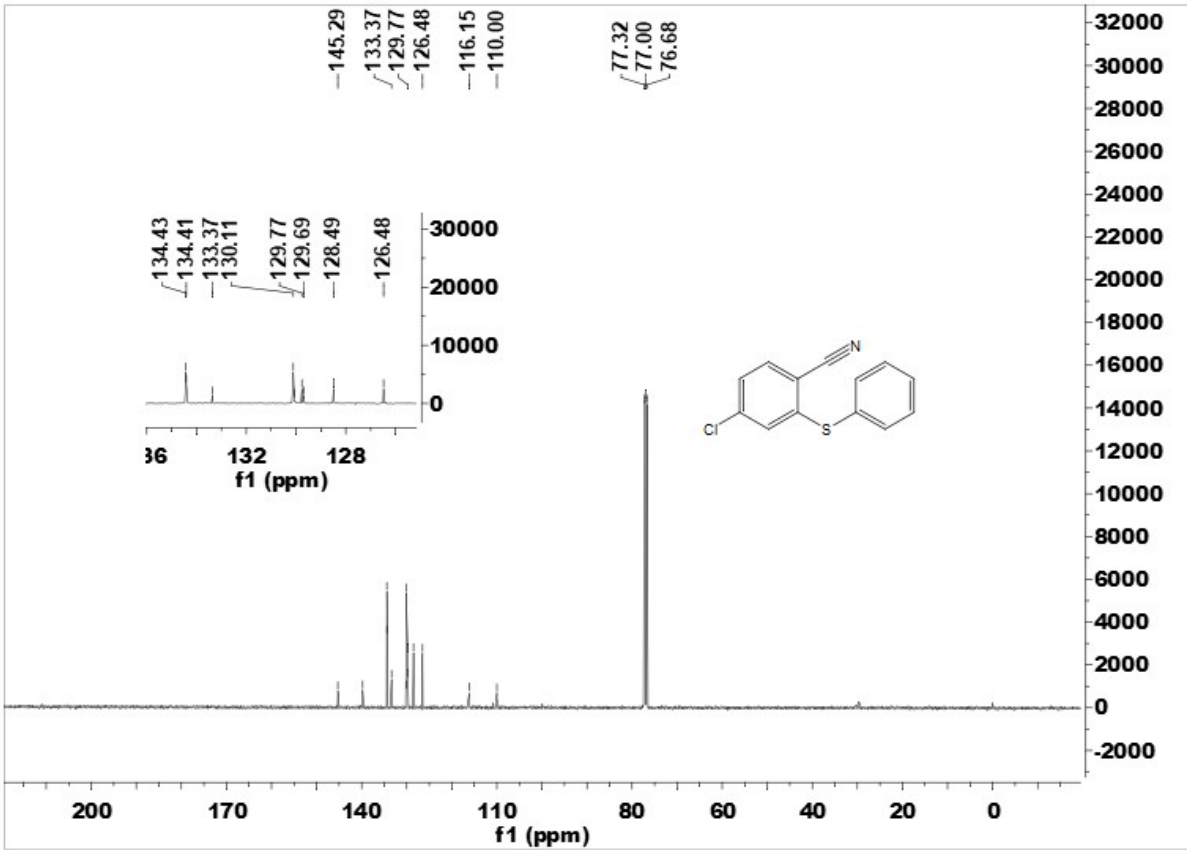




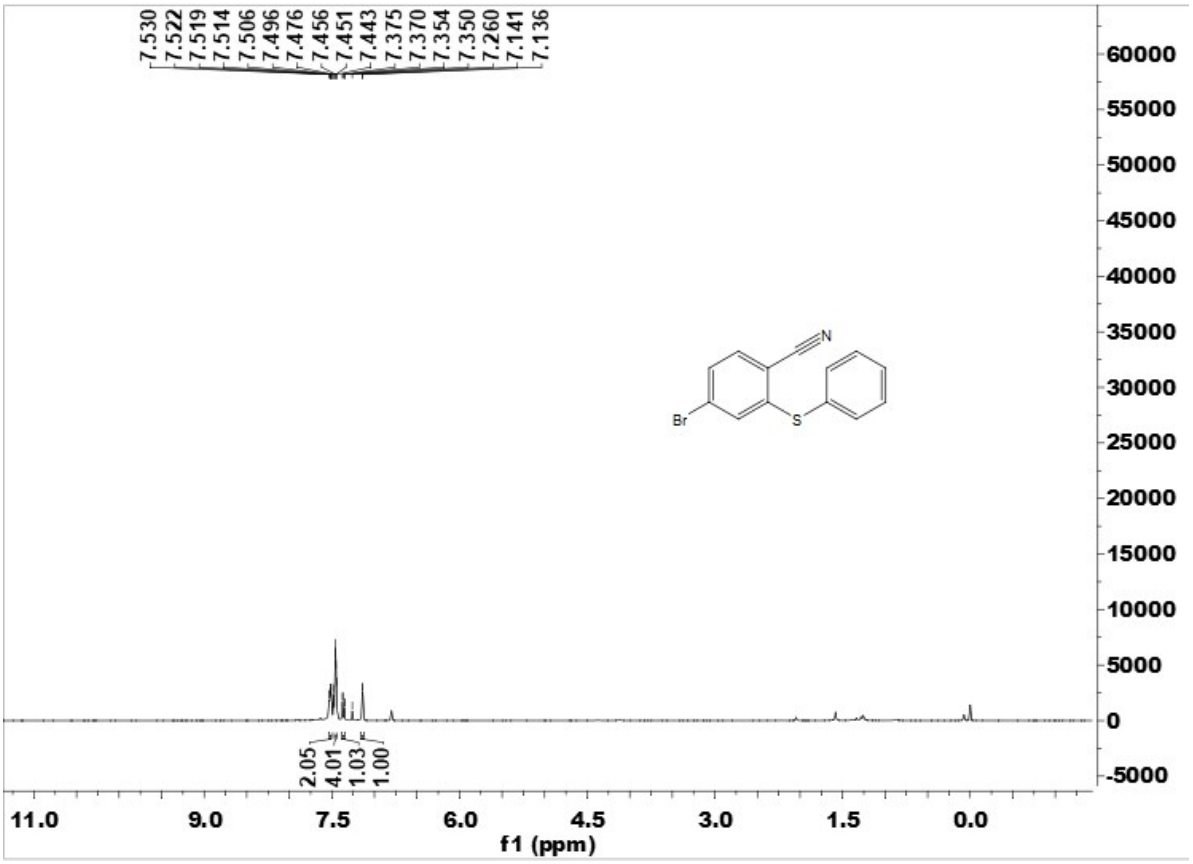


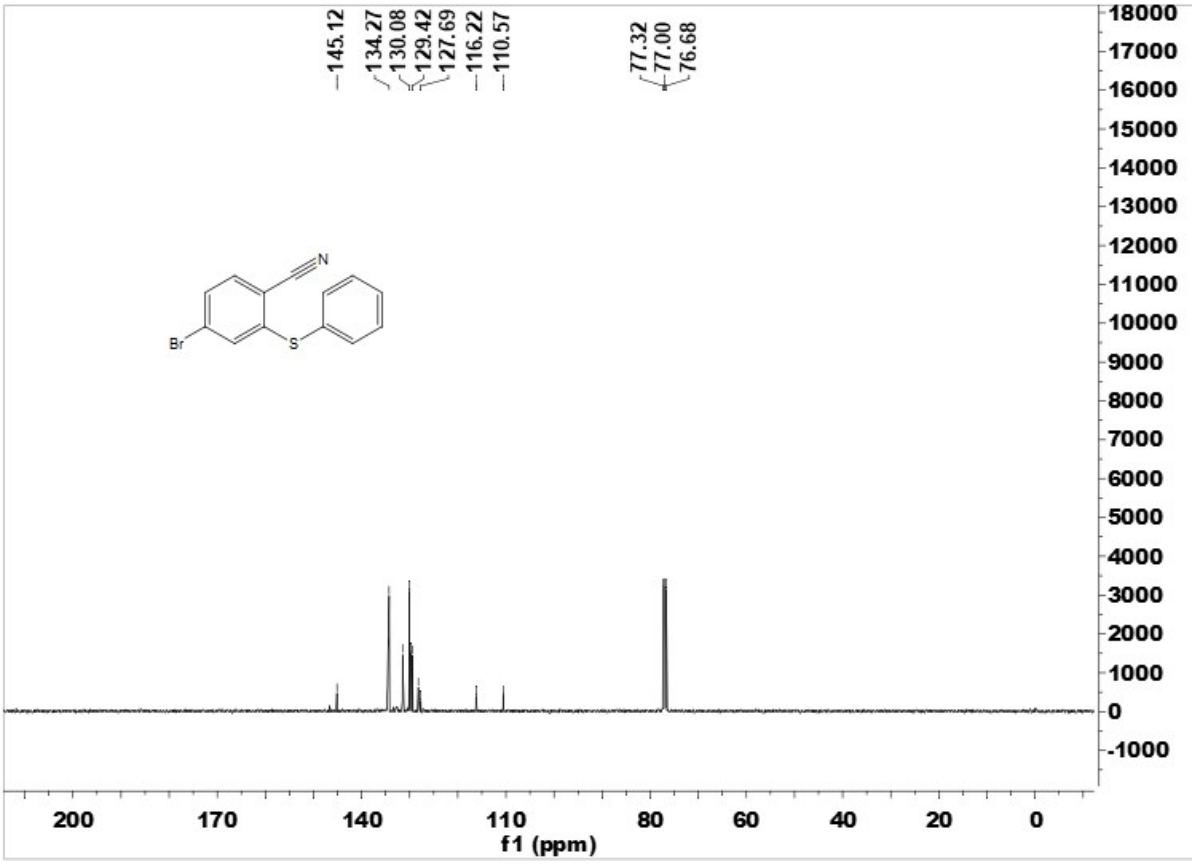
4-Chloro-2-(phenylthio)benzonitrile (3c)



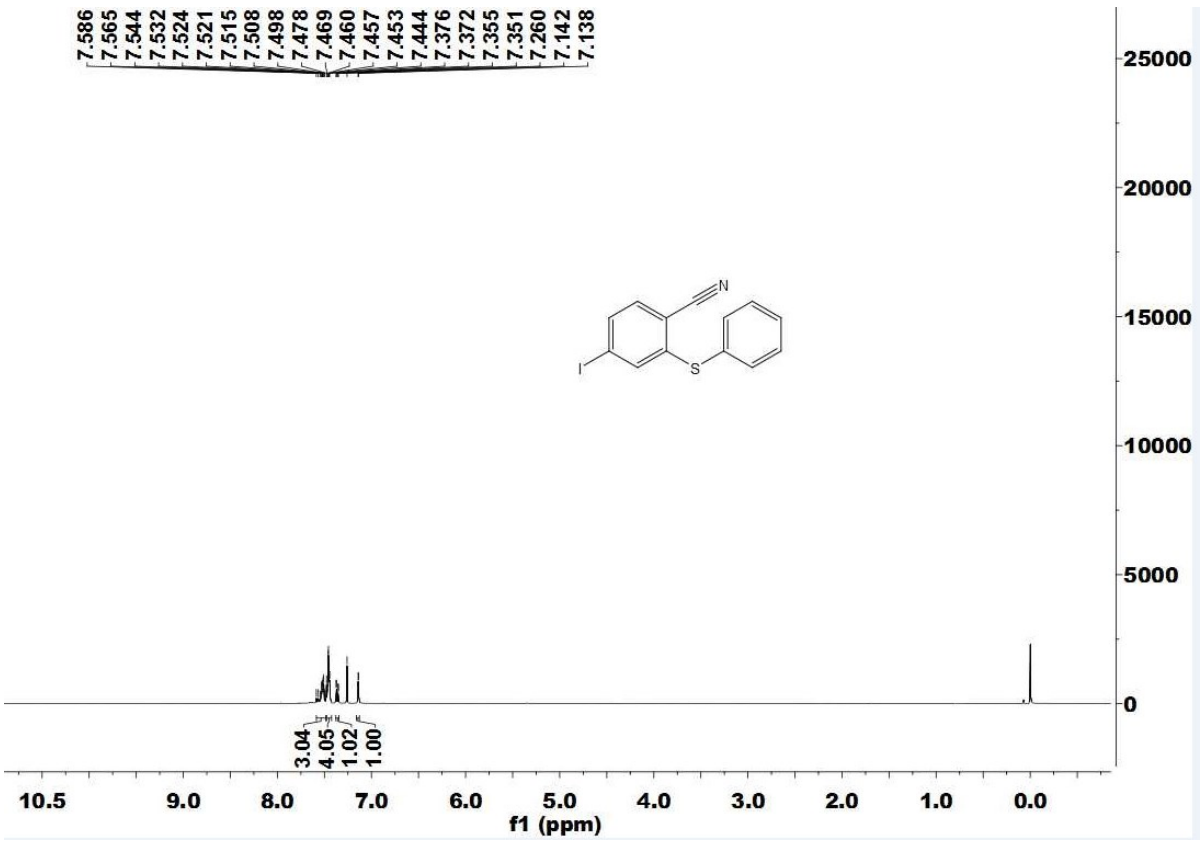


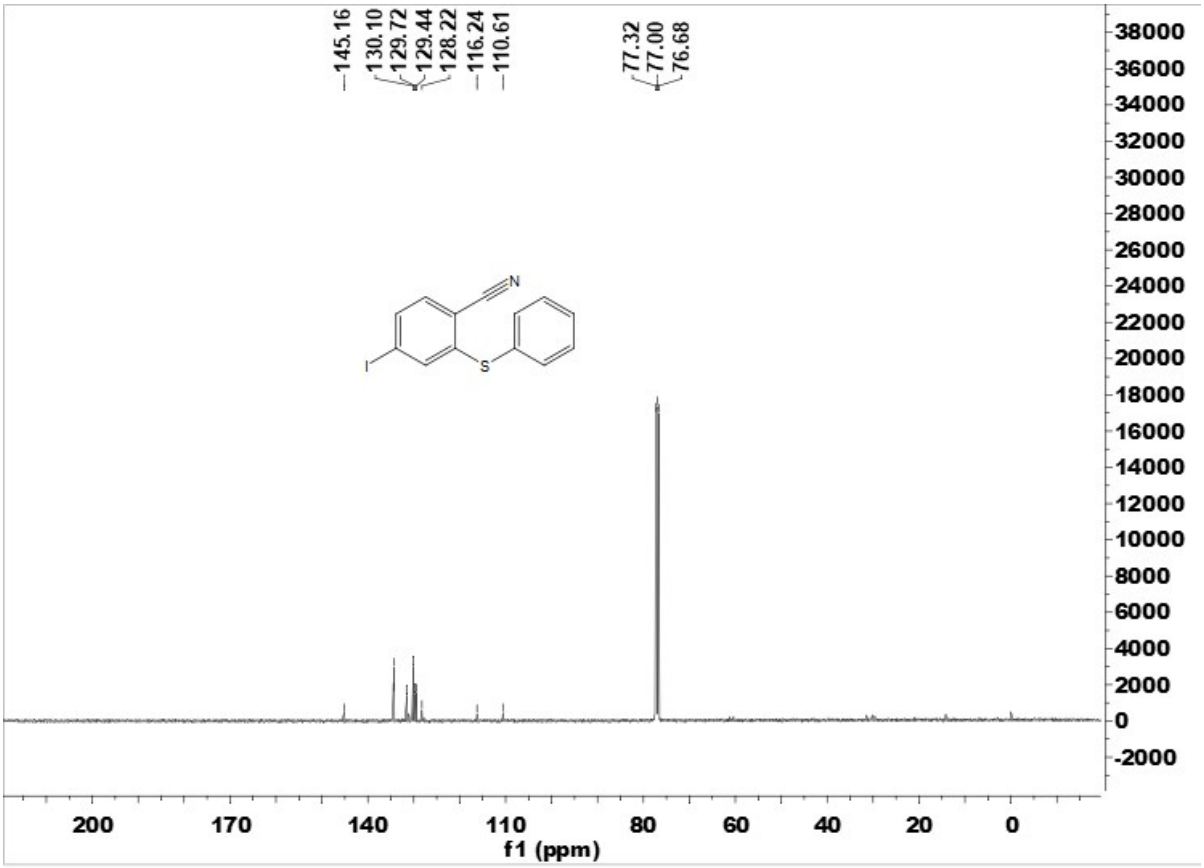
4-Bromo-2-(phenylthio)benzonitrile (3d)



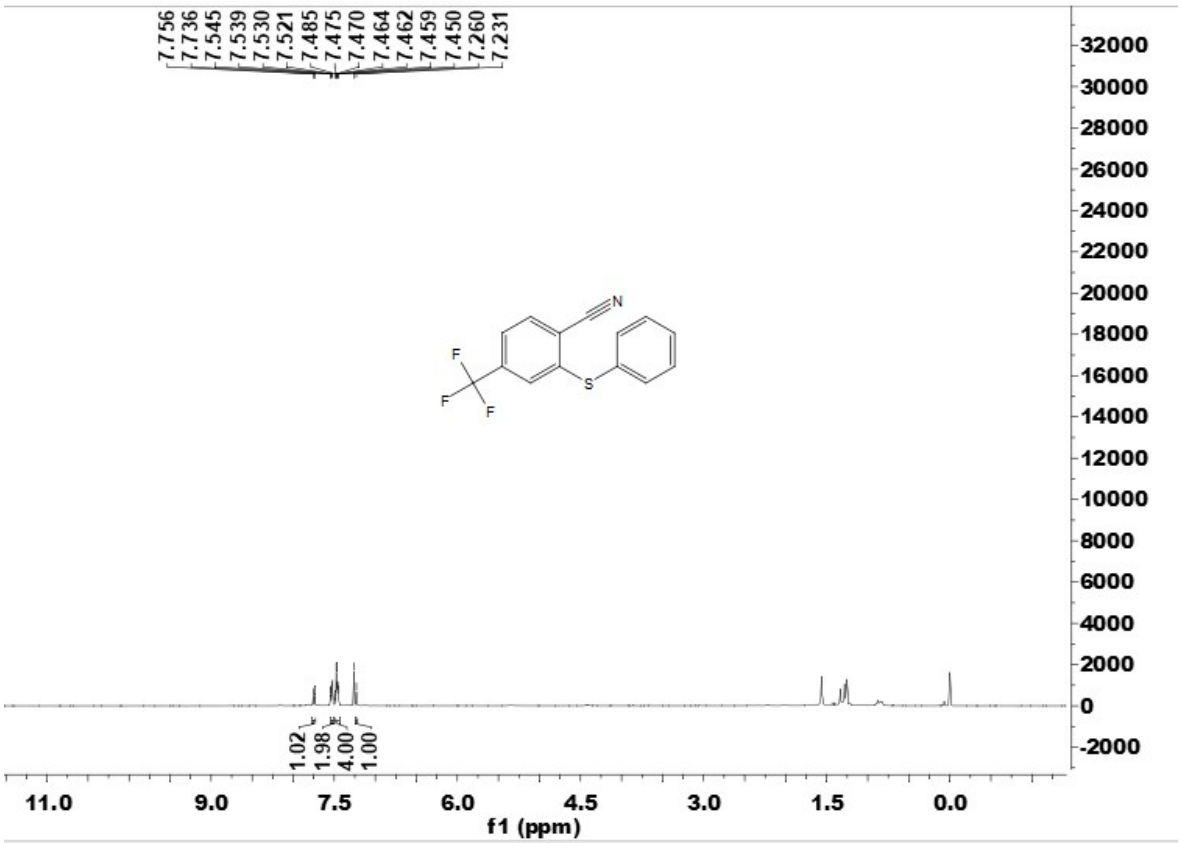


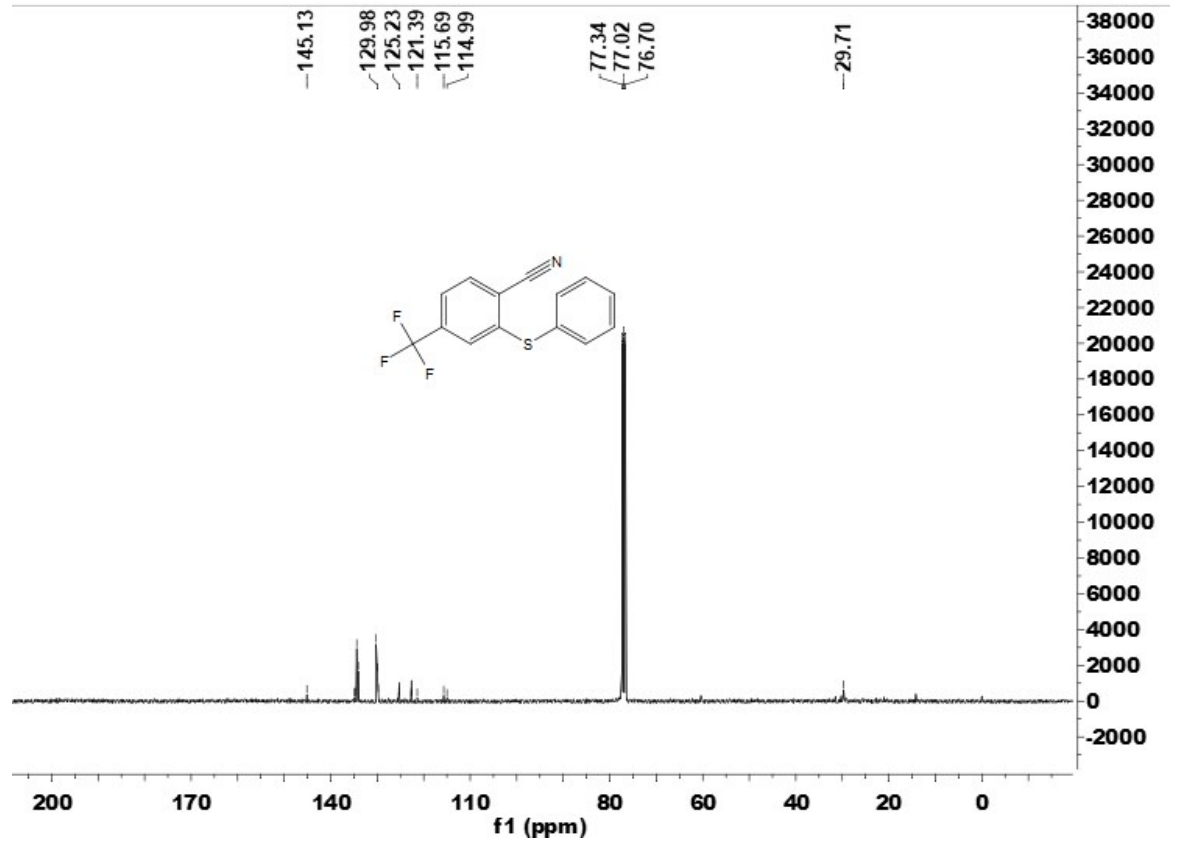
4-Iodo-2-(phenylthio)benzonitrile (3e)

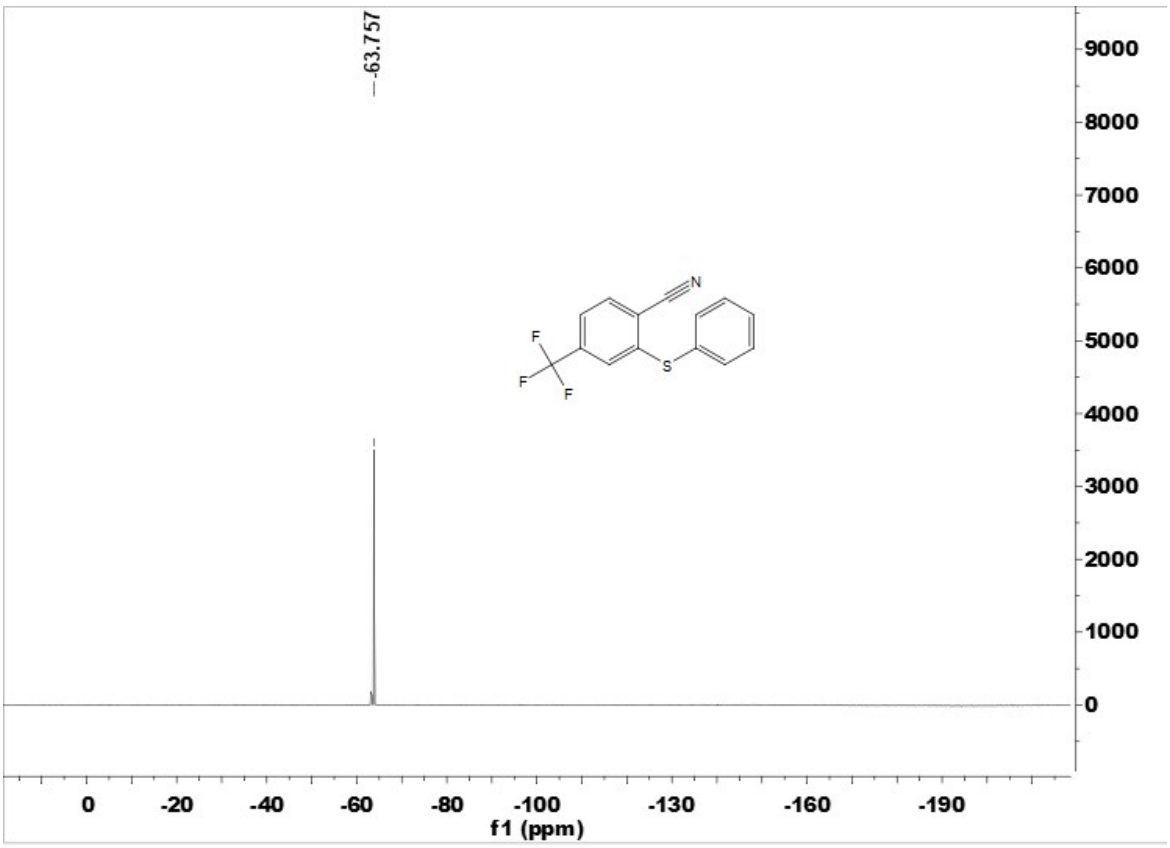




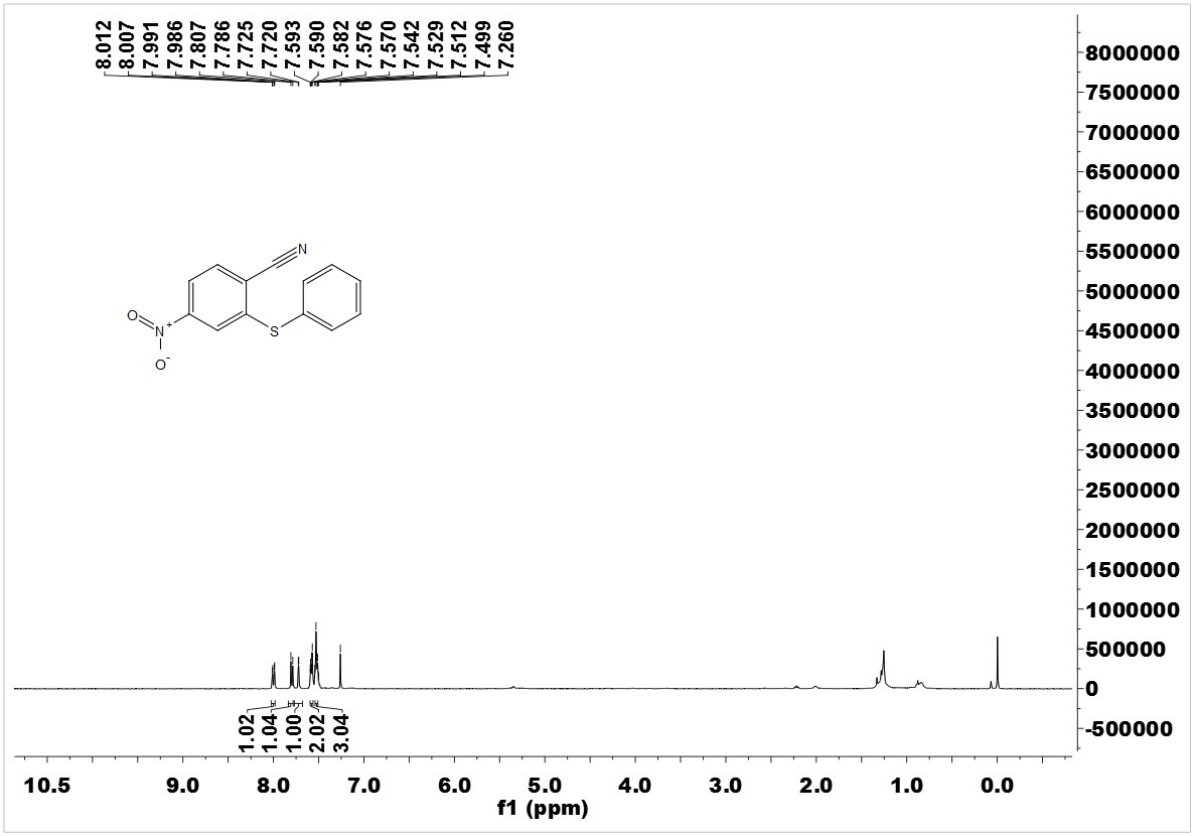
2-(Phenylthio)-4-(trifluoromethyl)benzonitrile (3f)

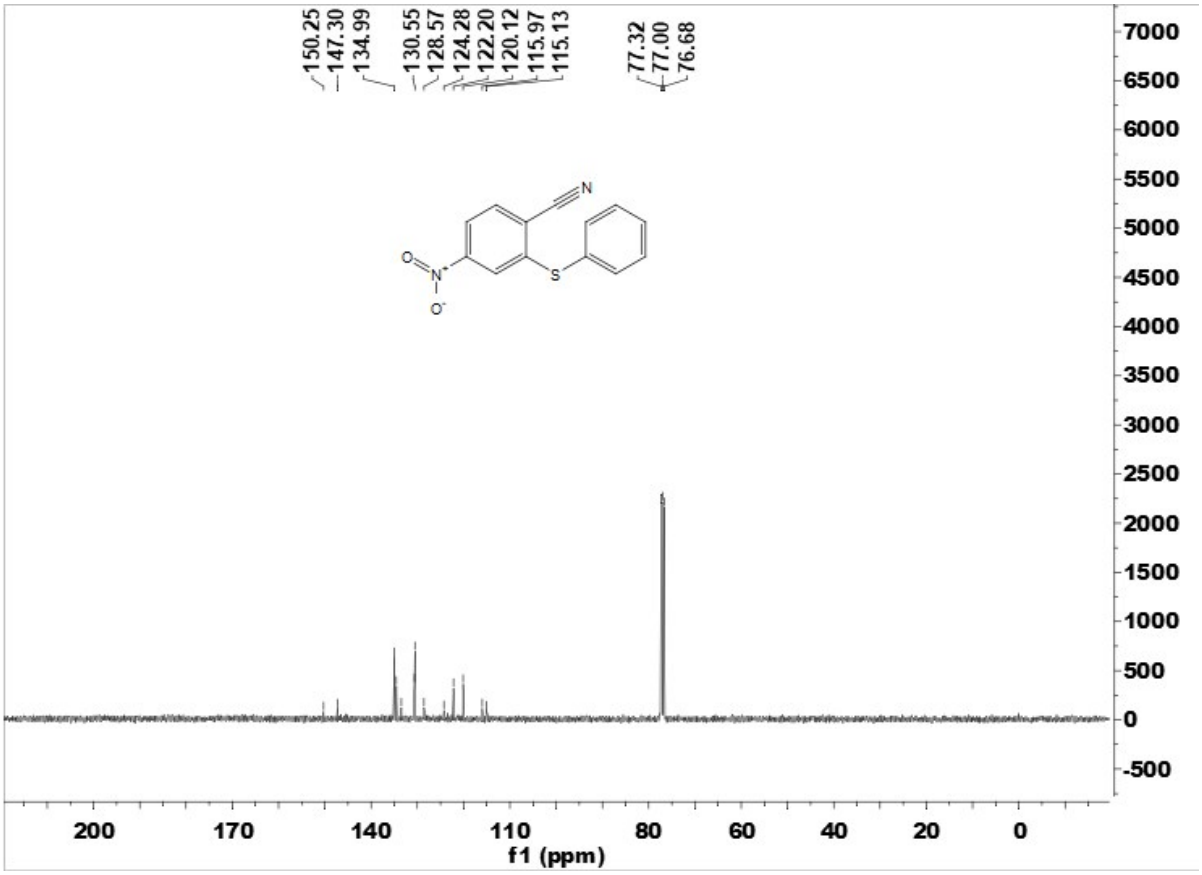

7.756
7.736
7.545
7.539
7.530
7.521
7.485
7.475
7.470
7.464
7.462
7.459
7.450
7.260
7.231
N
F
F
F
S
1.02
1.98
4.00
1.00
11.0
9.0
7.5
6.0
4.5
3.0
1.5
0.0
f1 (ppm)


145.13
129.98
125.23
121.39
115.69
114.99
77.34
77.02
76.70
29.71
N
F
F
F
S
200
170
140
110
80
60
40
20
0
f1 (ppm)

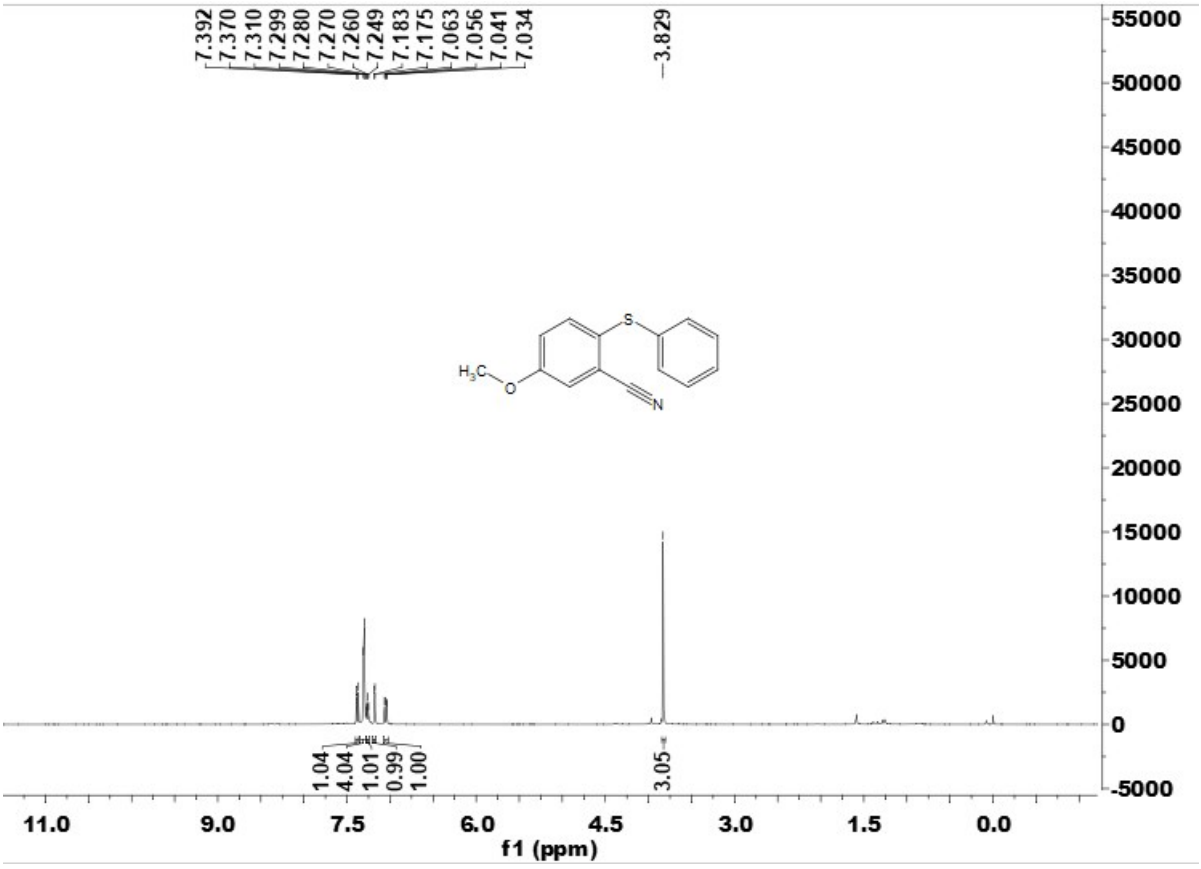


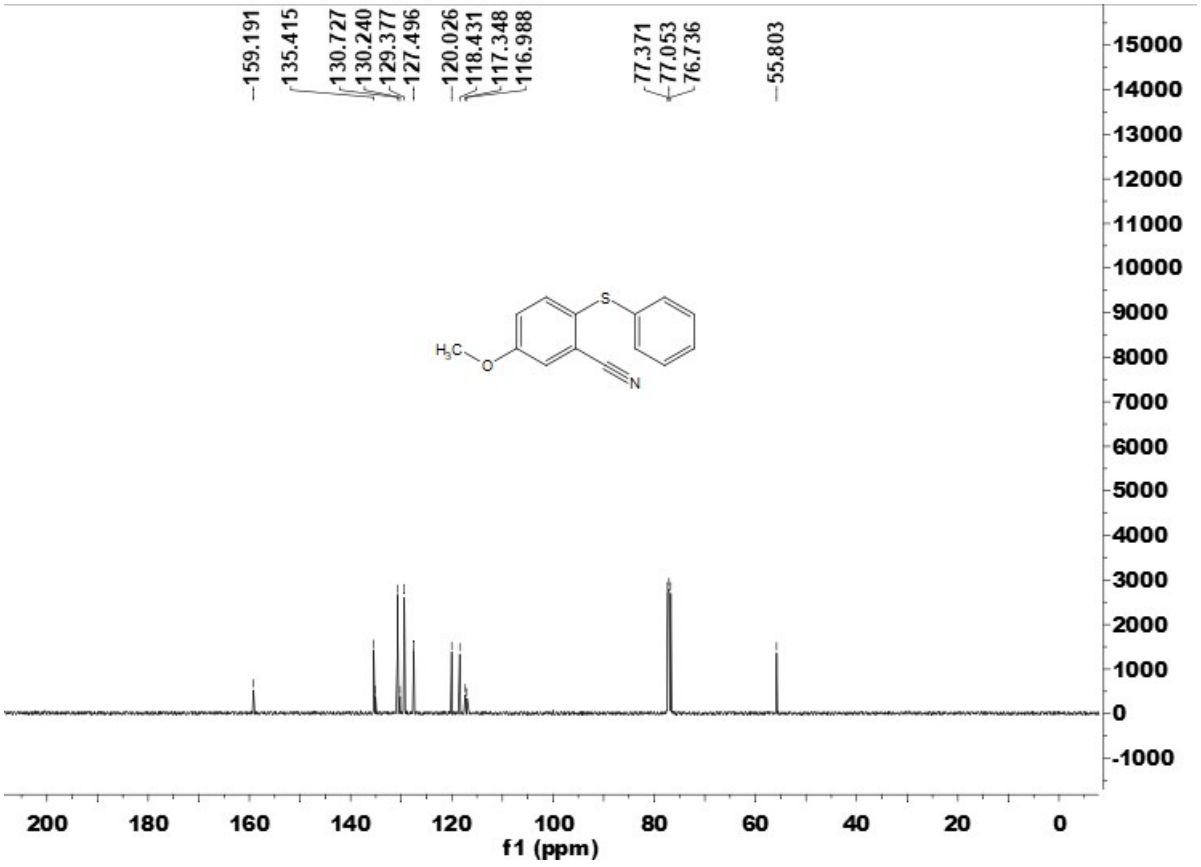
4-Nitro-2-(phenylthio)benzonitrile (3g)



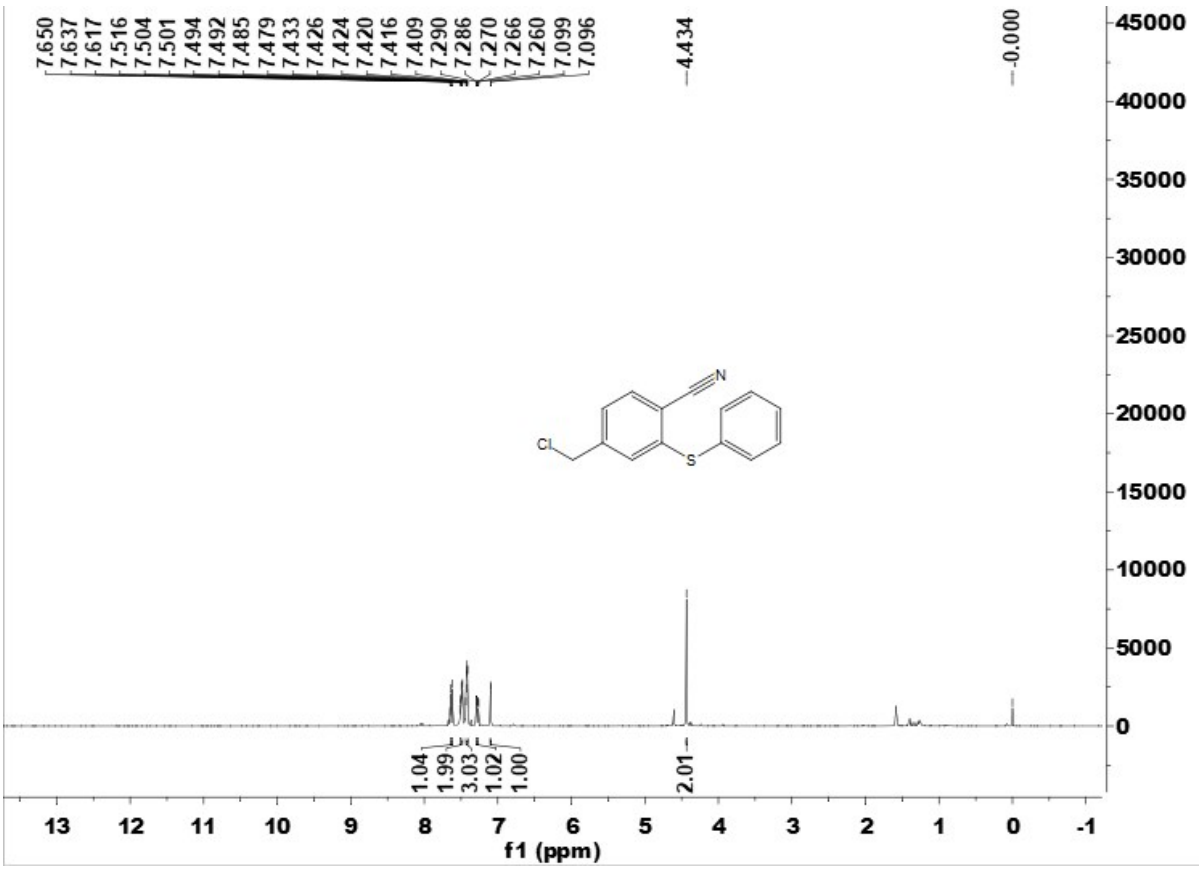


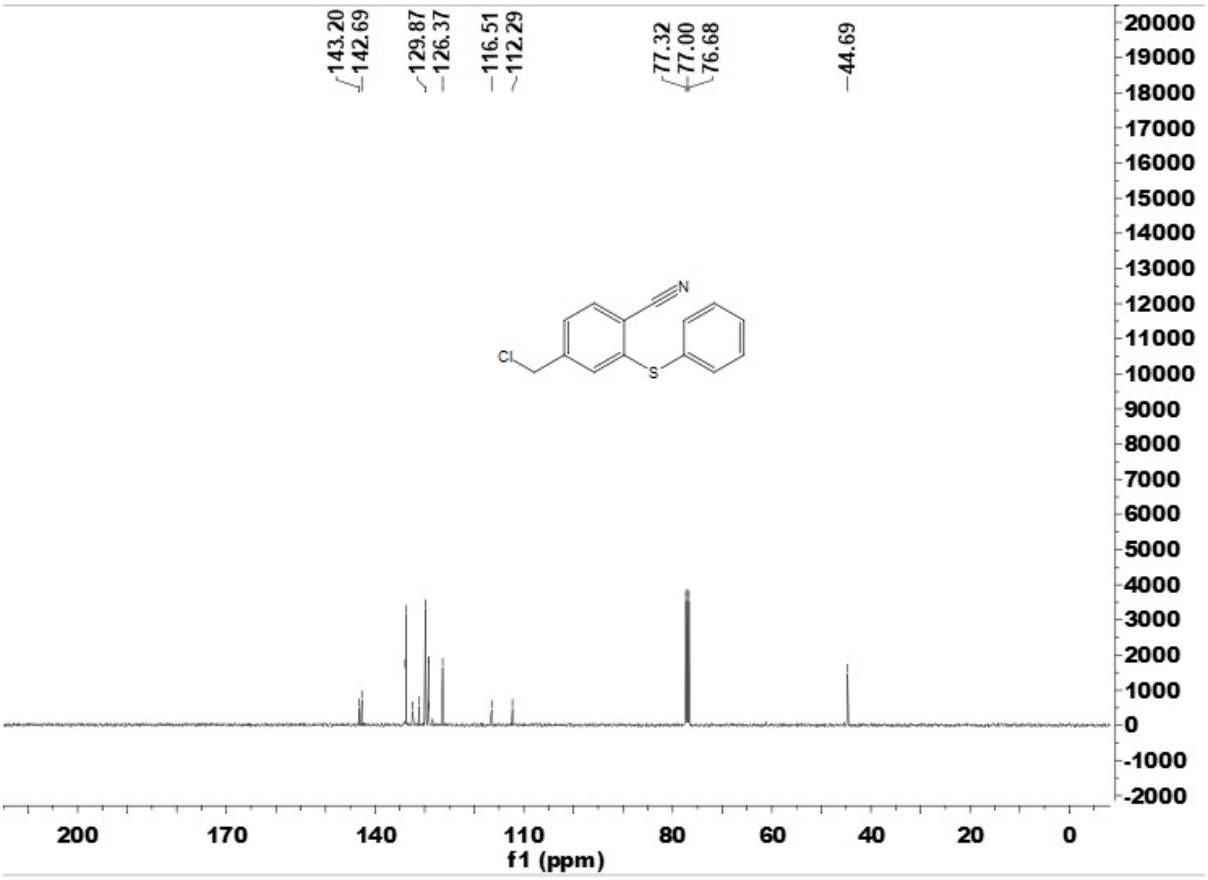
5-Methoxy-2-(phenylthio)benzonitrile (3h)



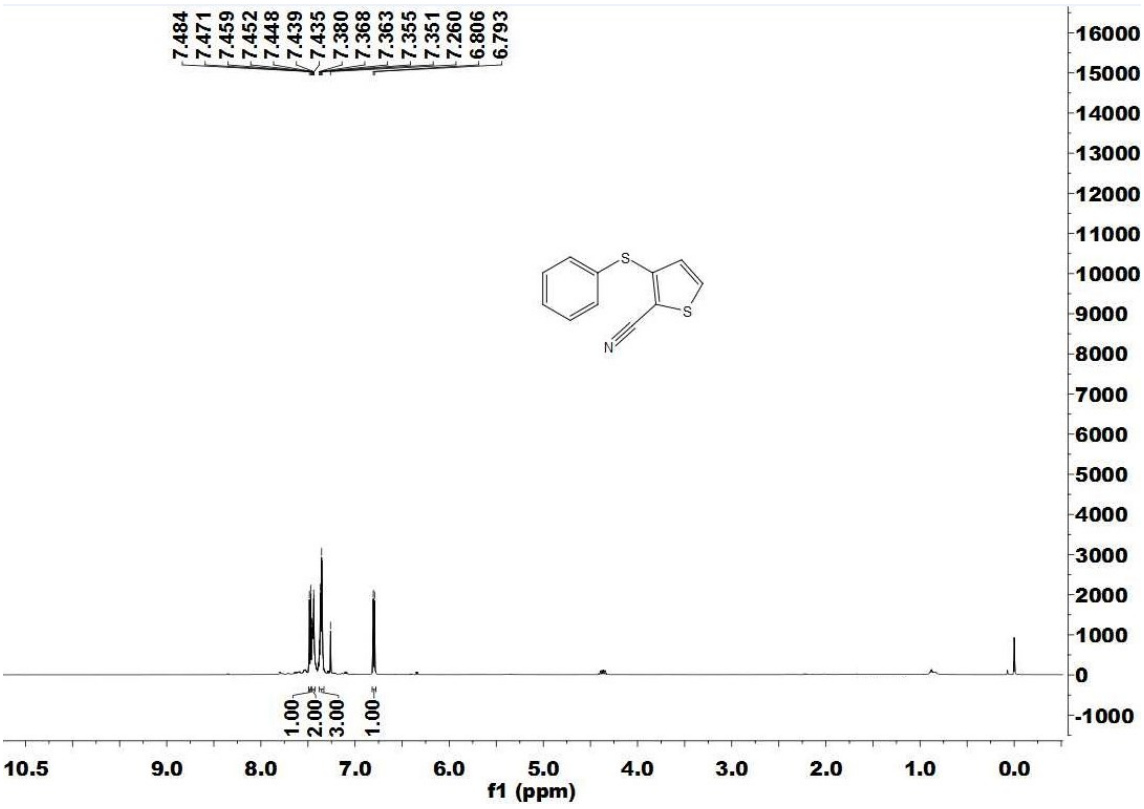


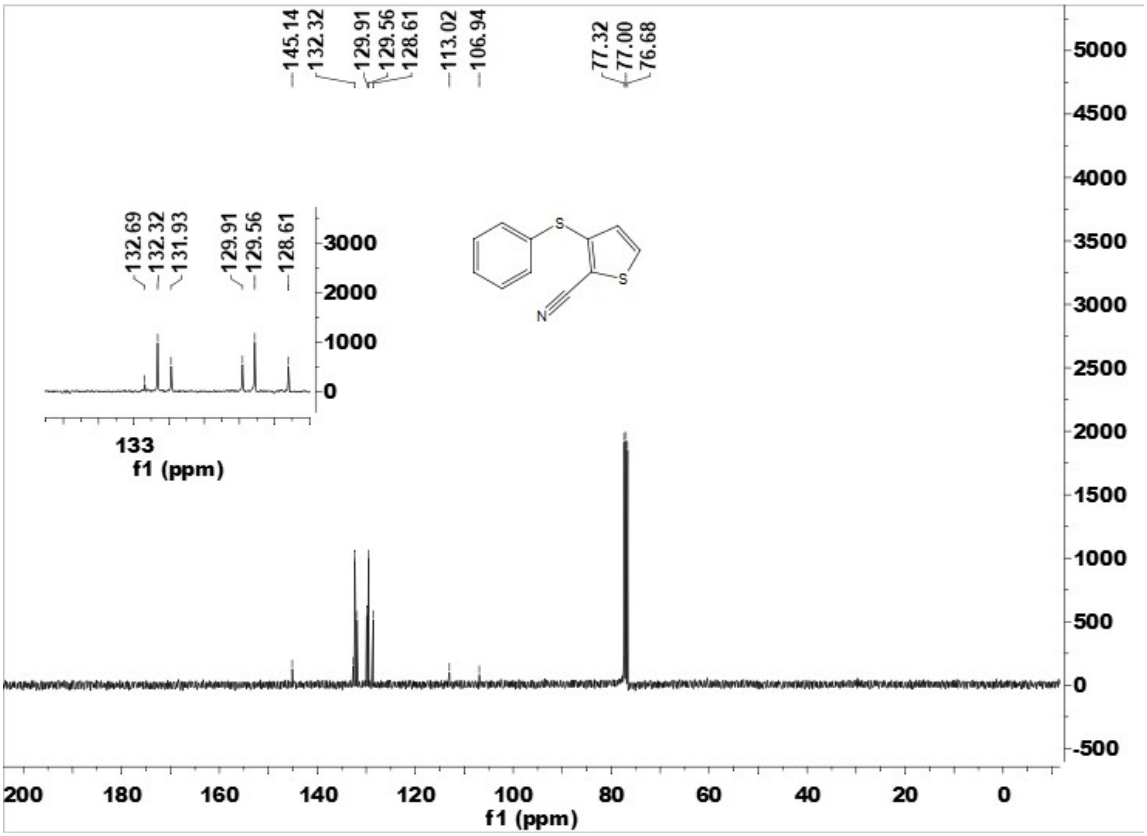
4-(Chloromethyl)-2-(phenylthio)benzonitrile (3i)



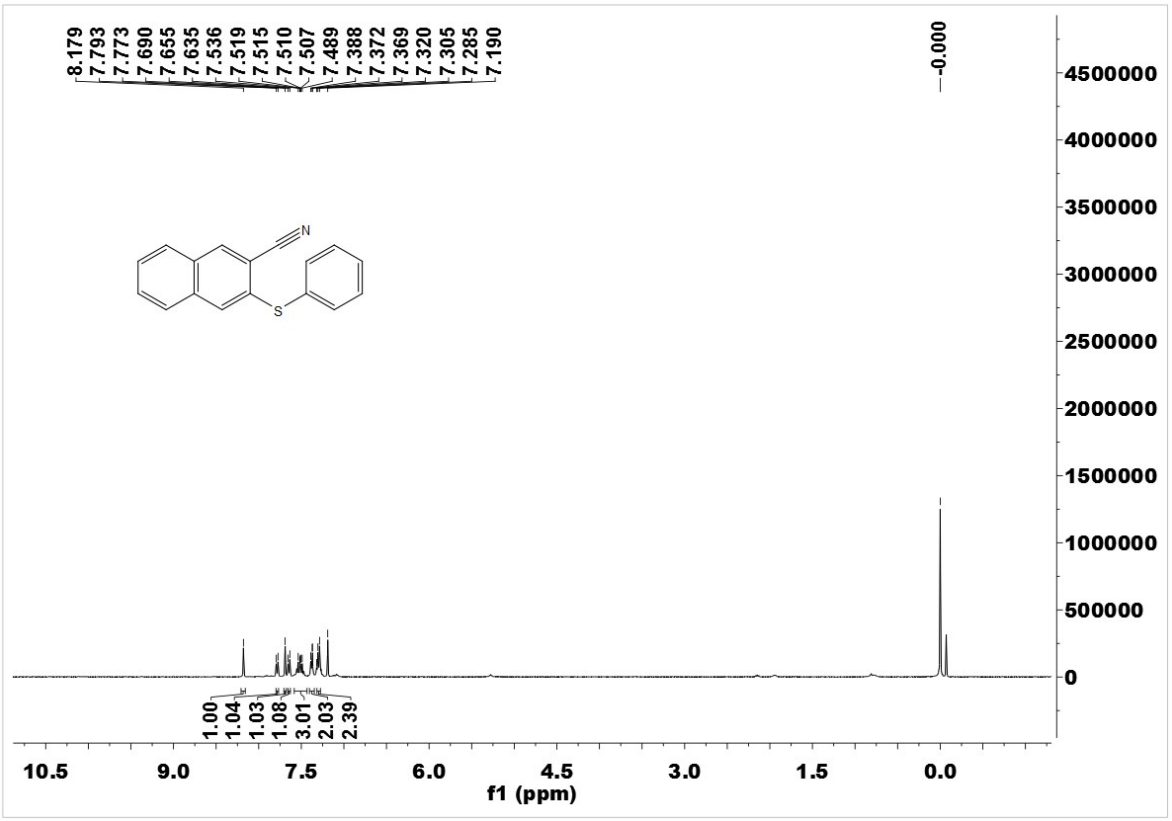


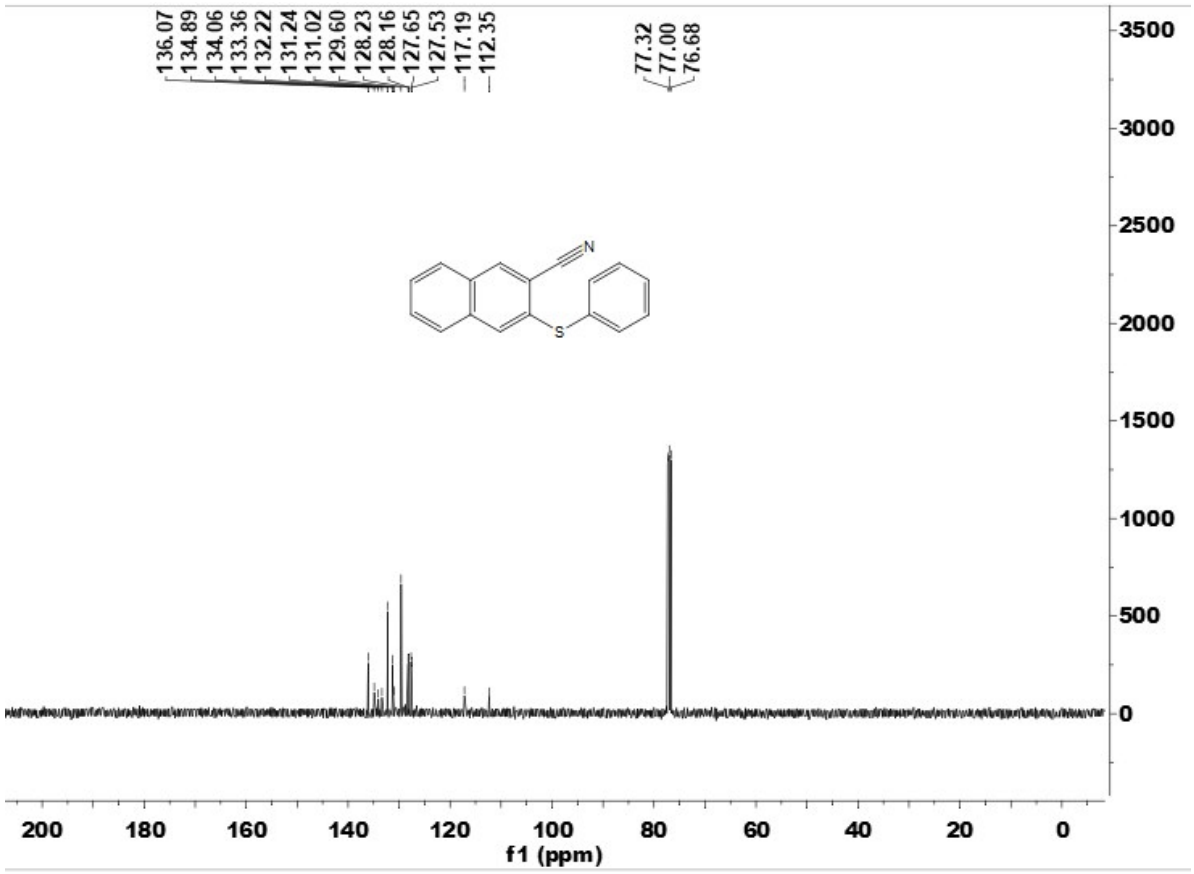
3-(Phenylthio)thiophene-2-carbonitrile (3j)



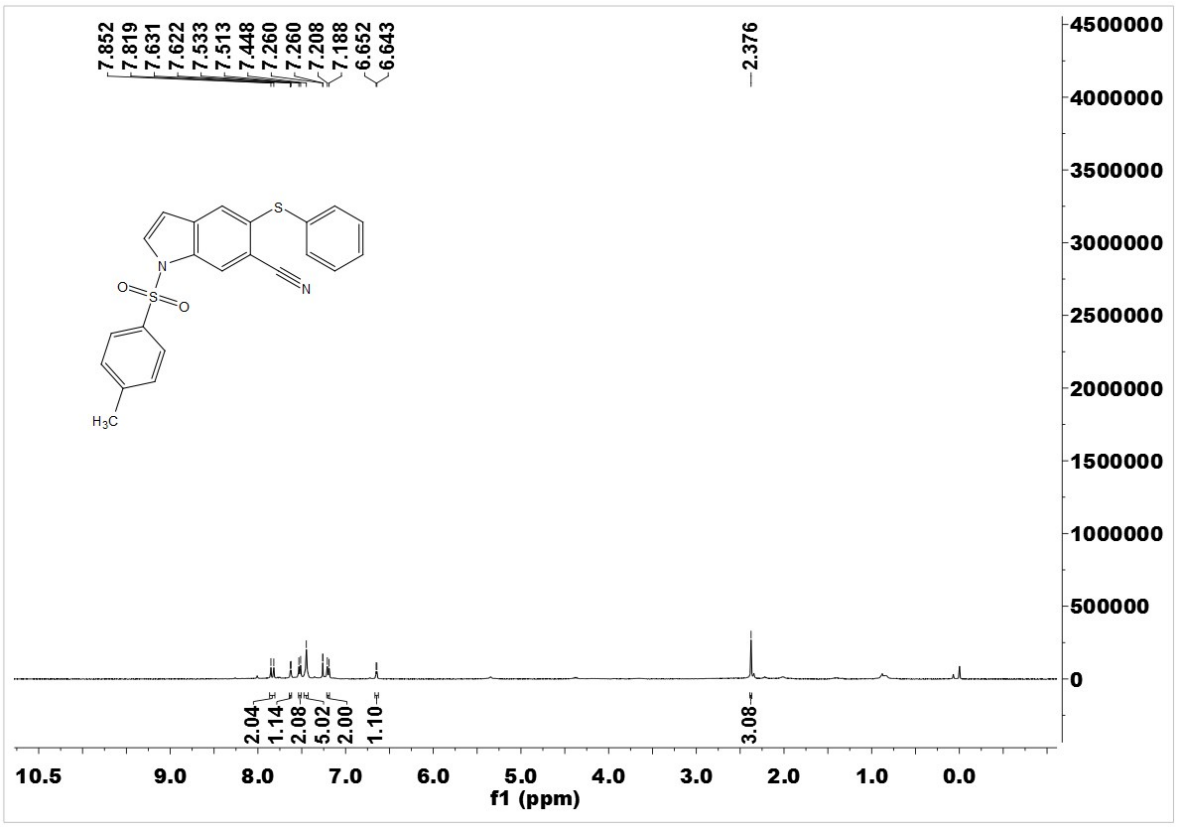


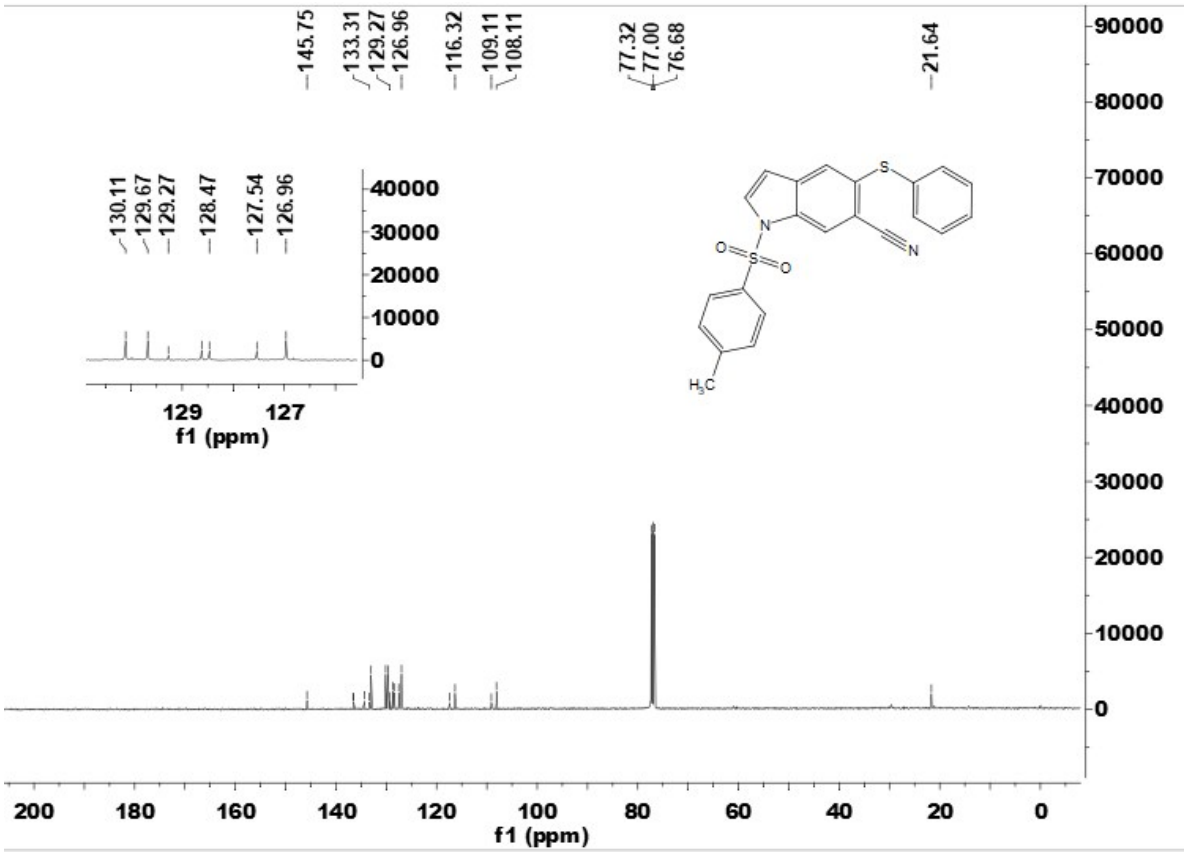
3-(Phenylthio)-2-naphthonitrile (3k)



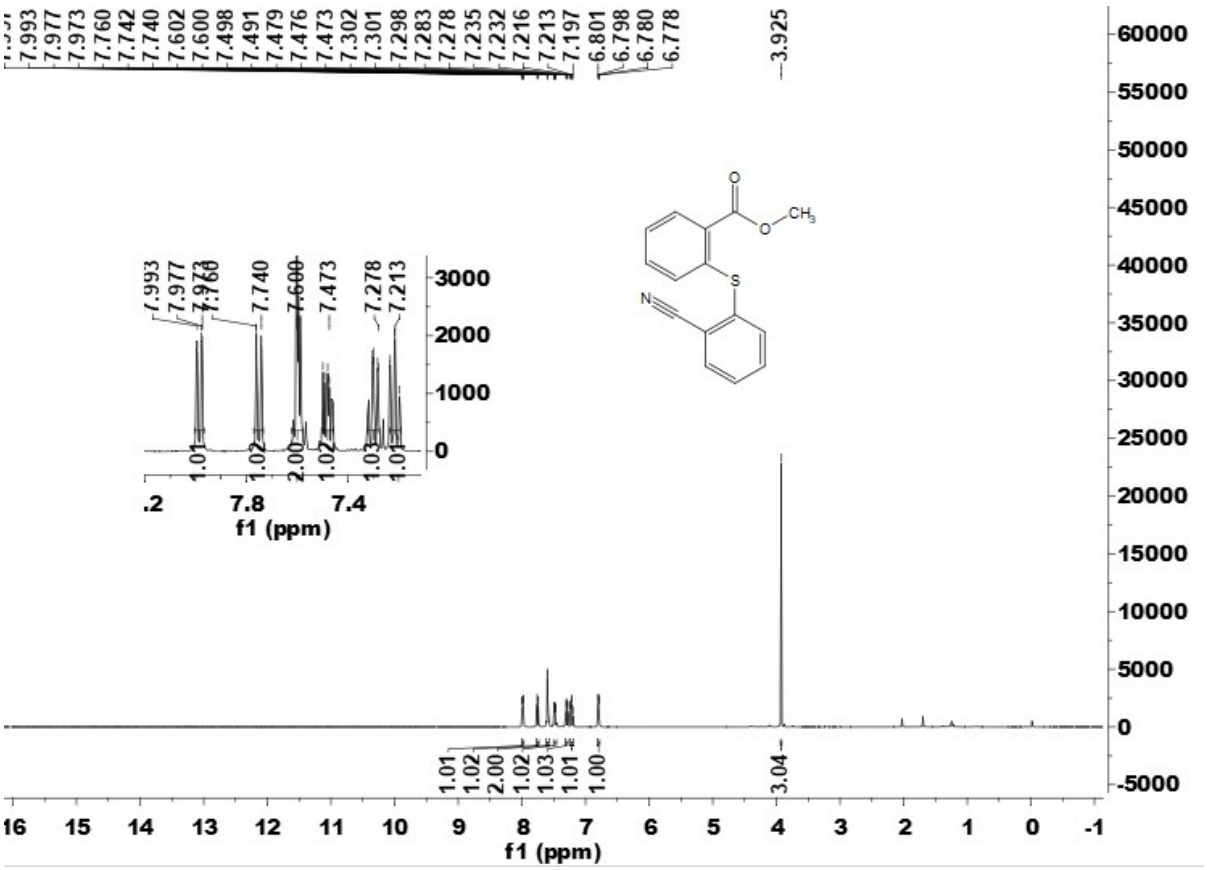


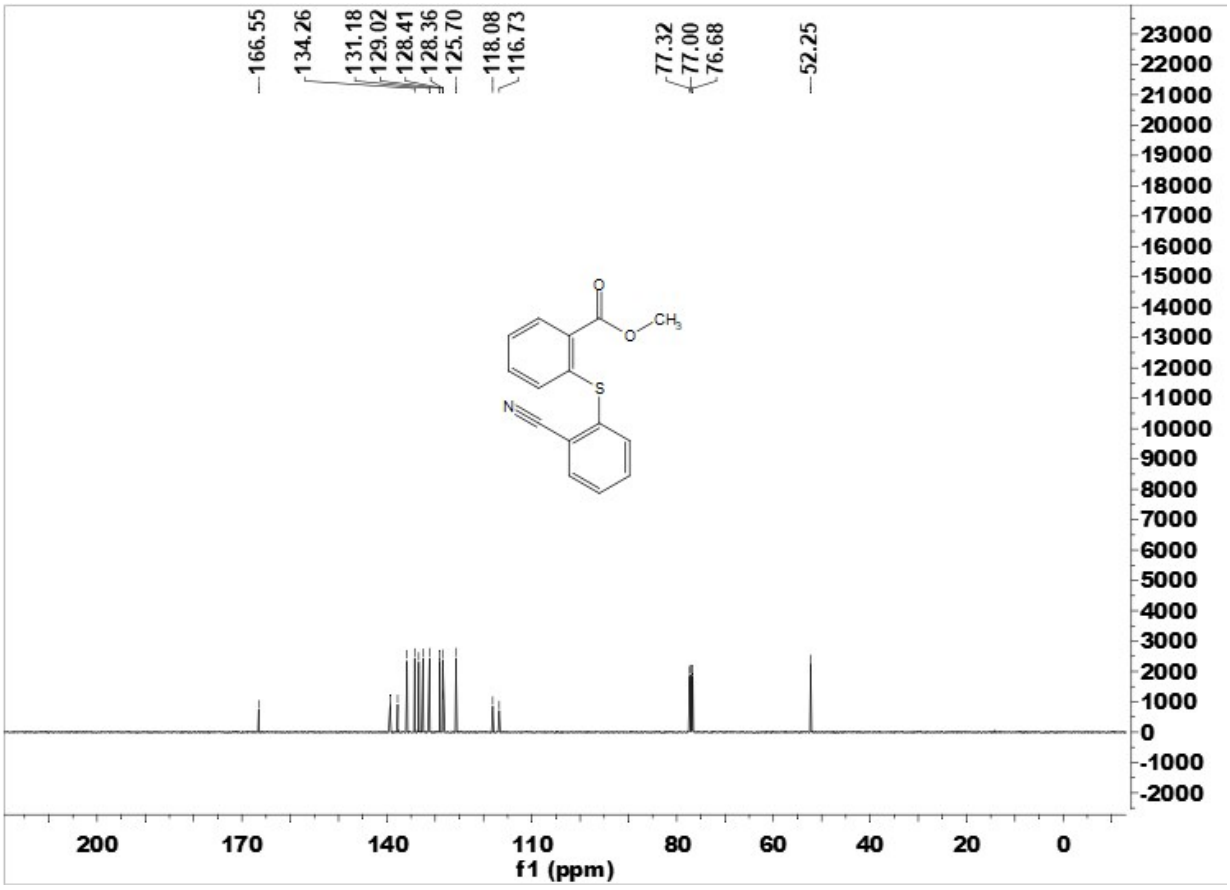
6-(Phenylthio)-1-tosyl-1*H*-indole-5-carbonitrile (3l)



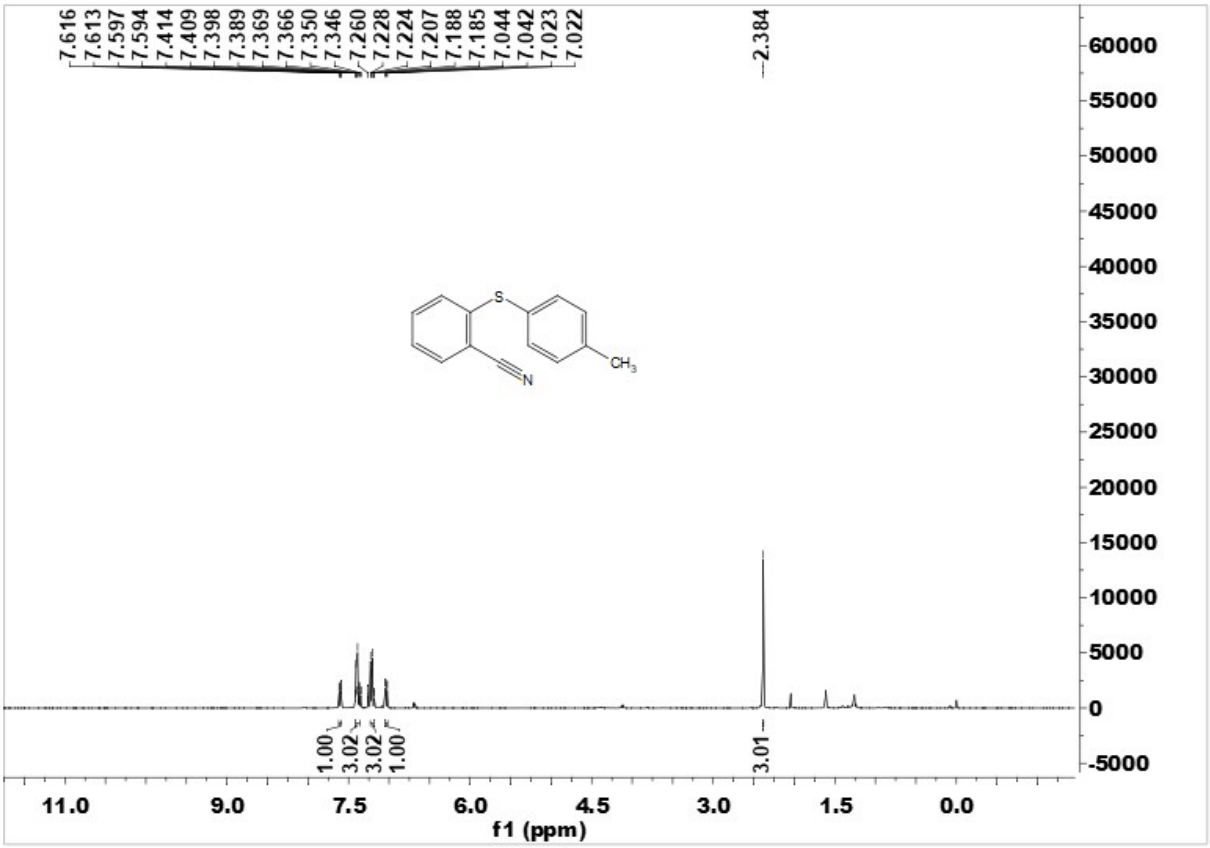


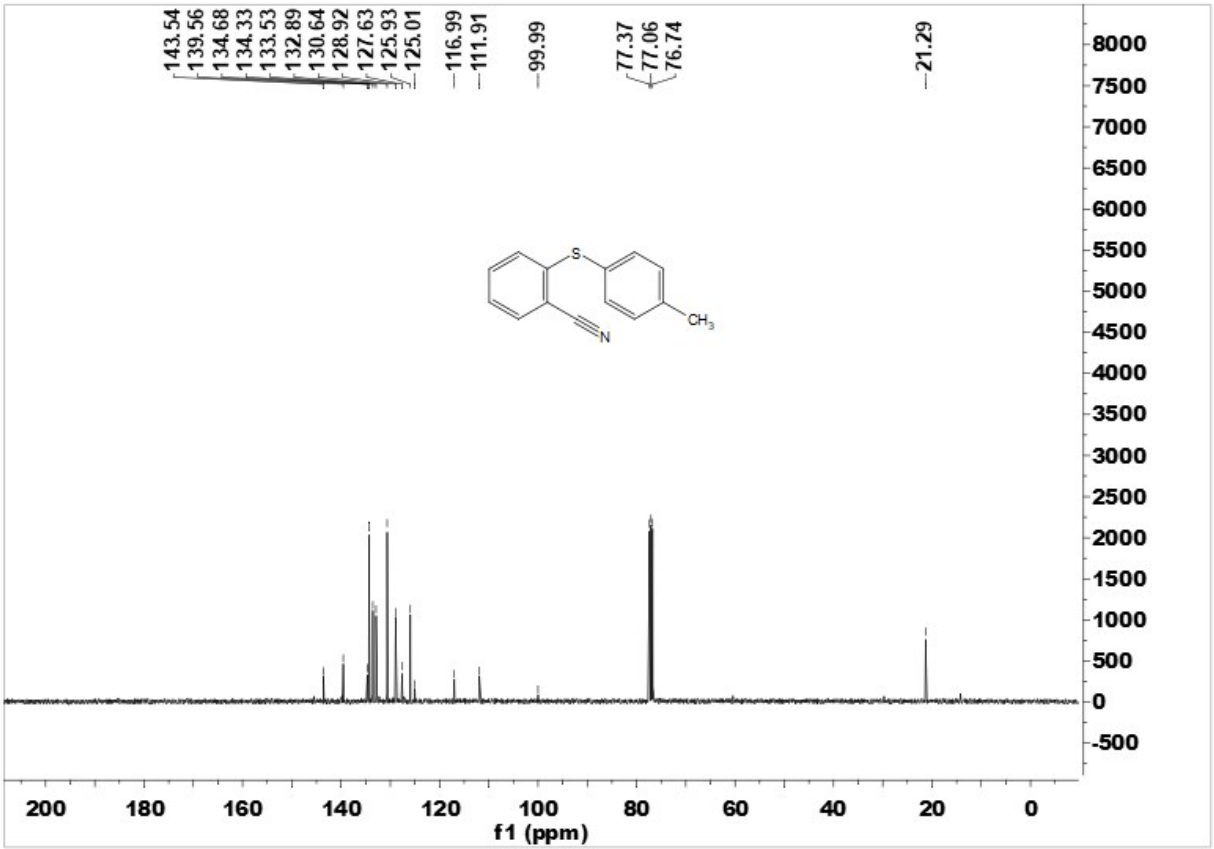
Methyl 2-((2-cyanophenyl)thio)benzoate (3m)



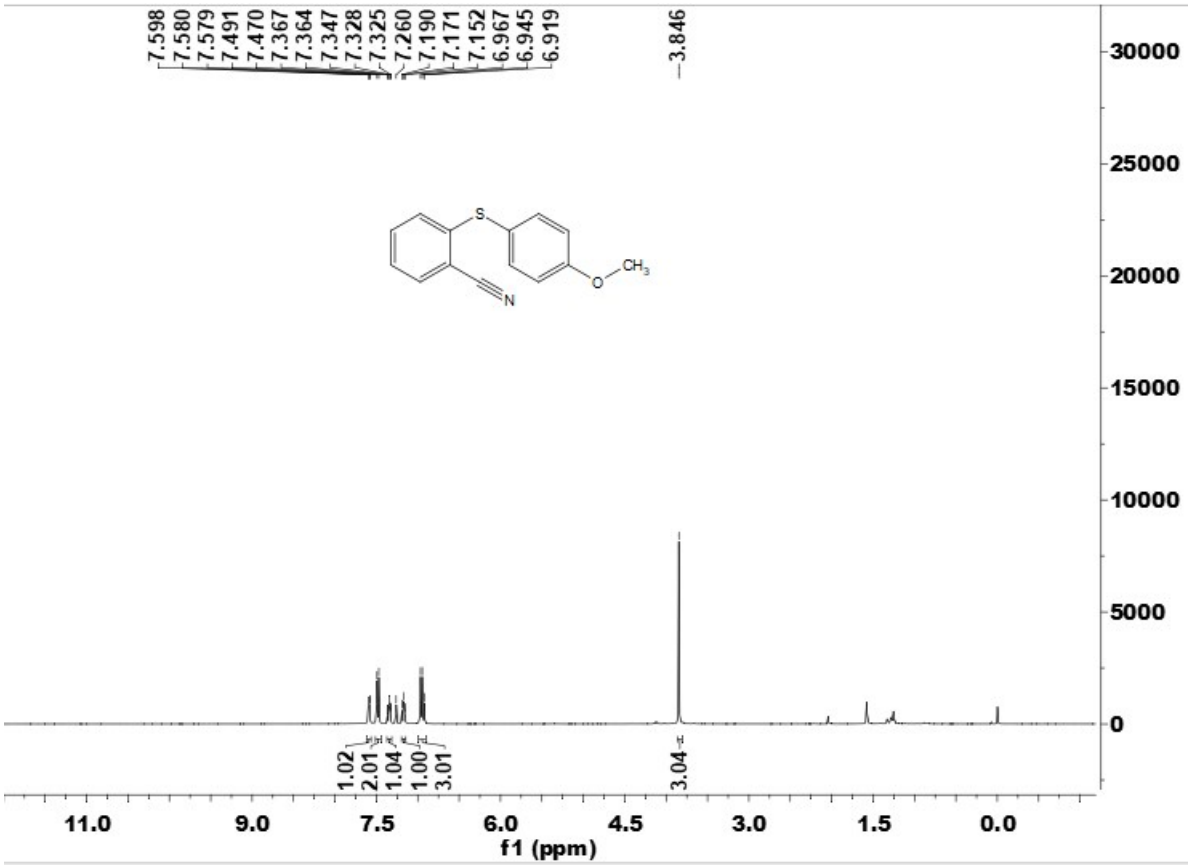


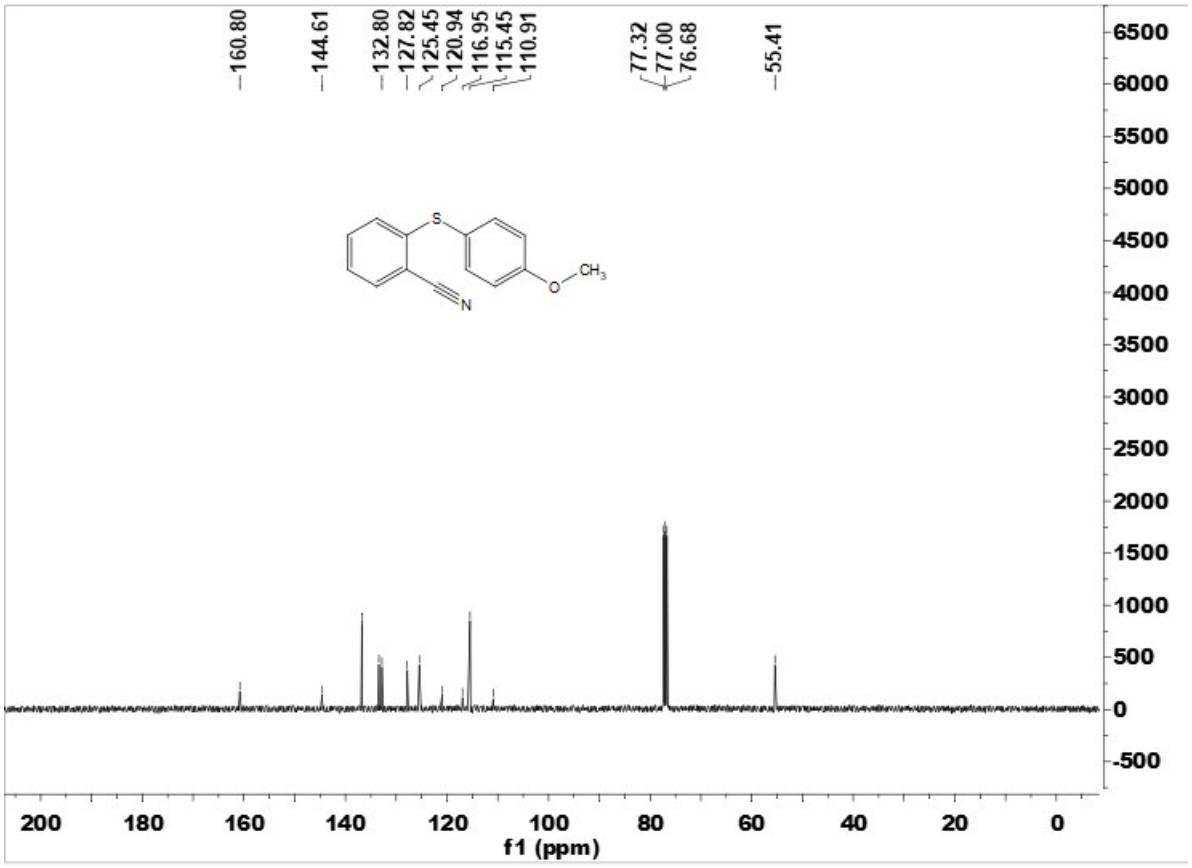
2-(*p*-Tolylthio)benzonitrile (3n)



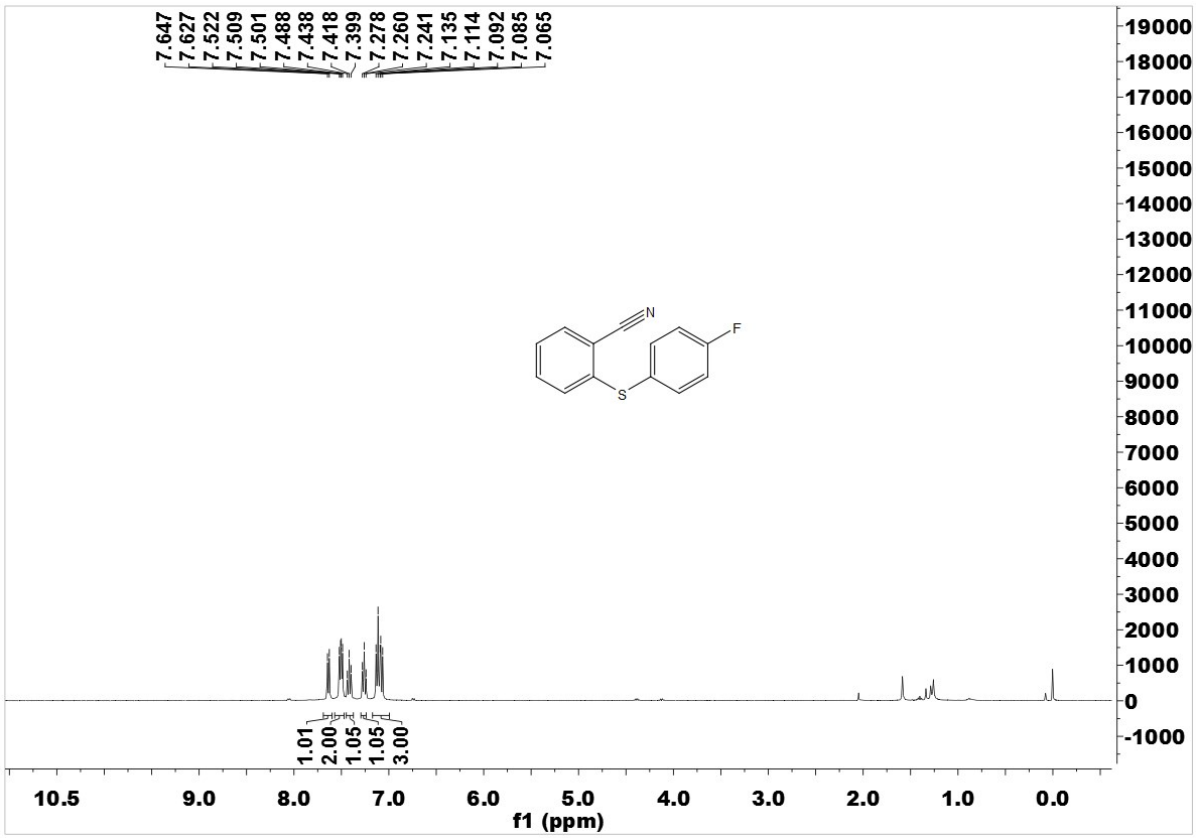


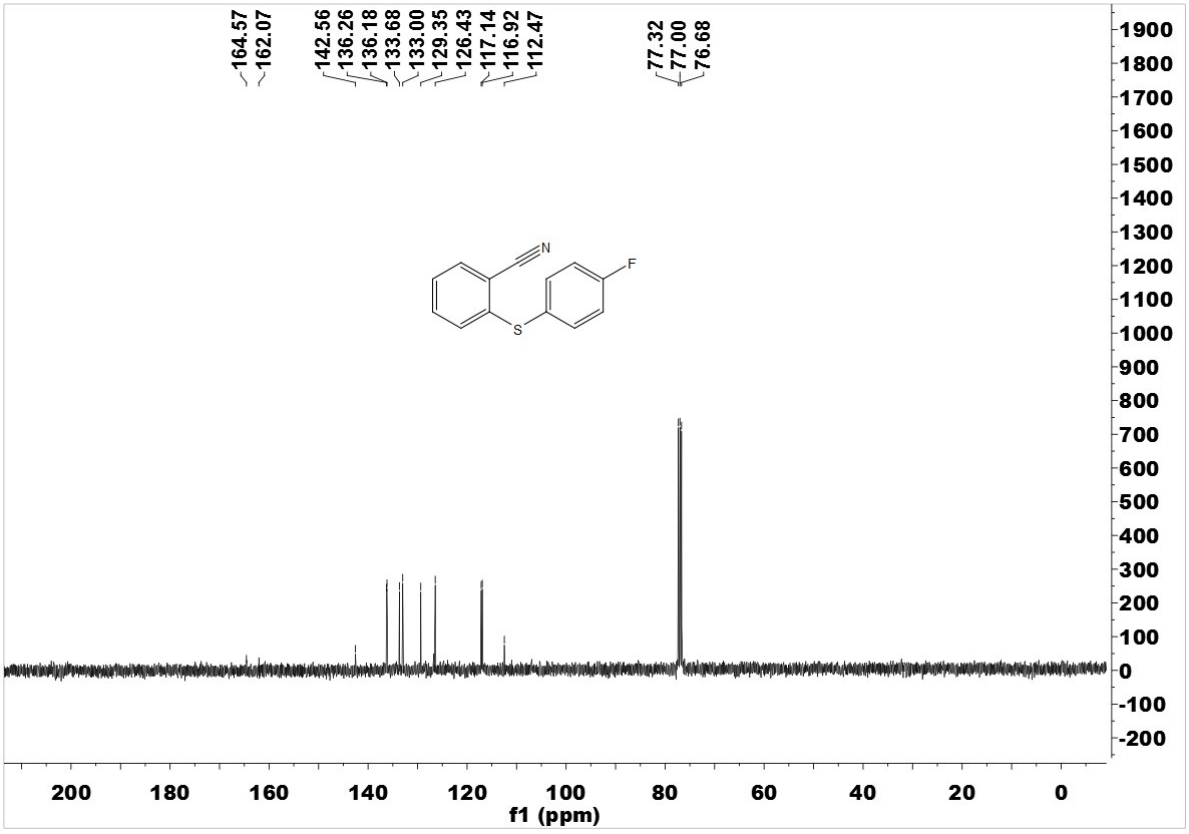
5-Methoxy-2-(phenylthio)benzonitrile (3o)

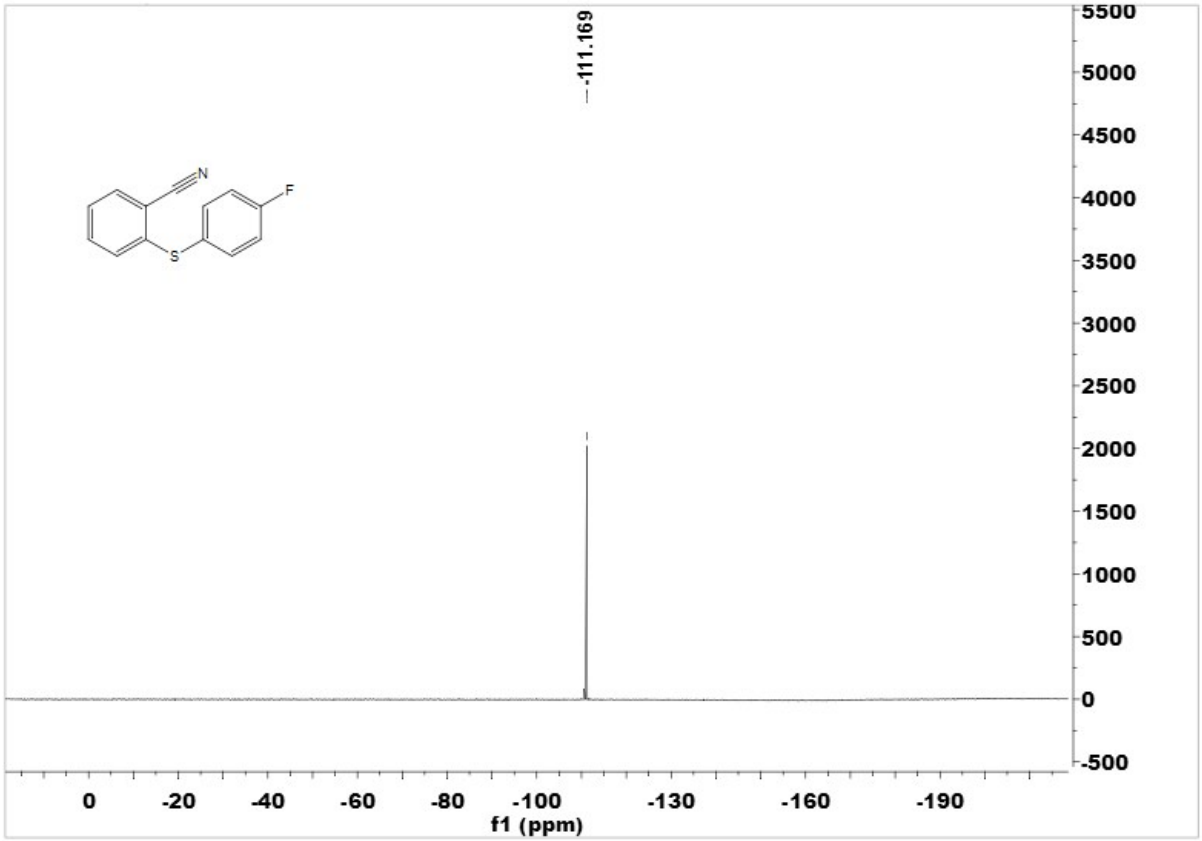




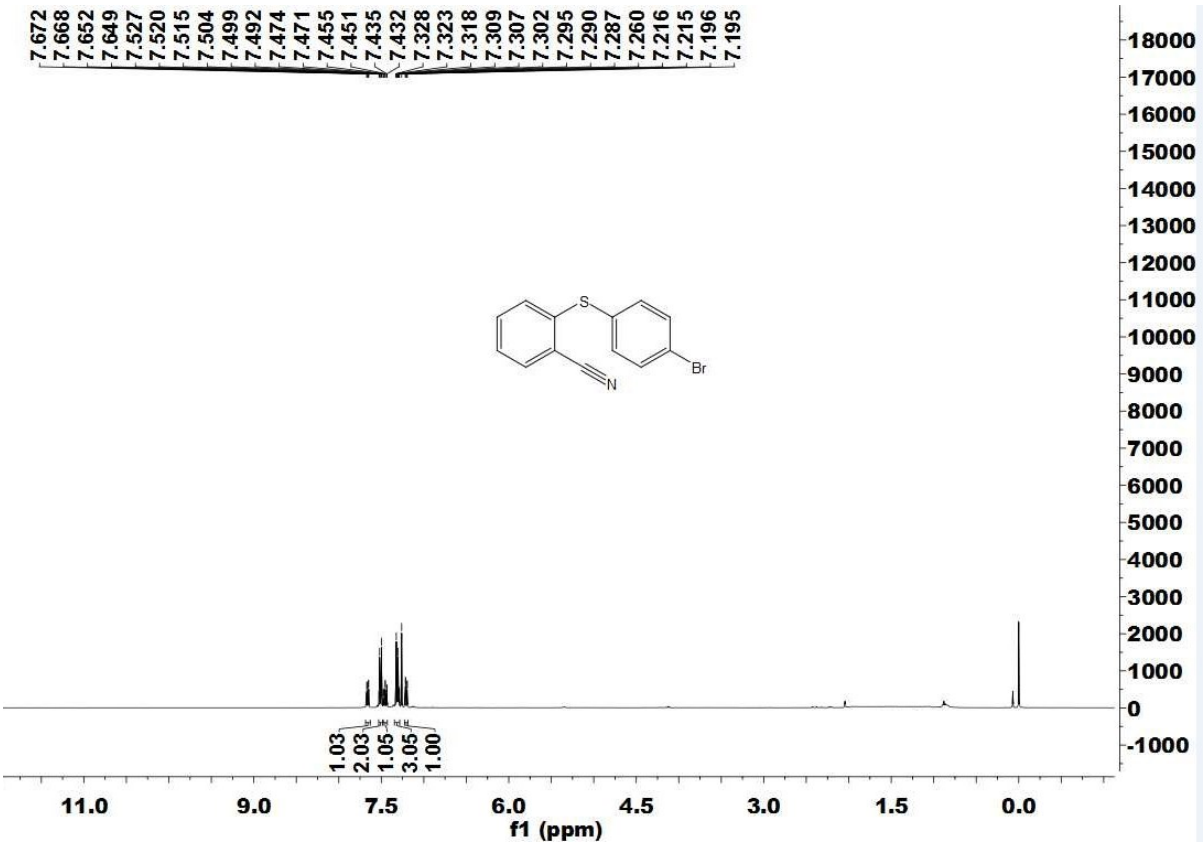
2-((4-Fluorophenyl)thio)benzonitrile (3p)

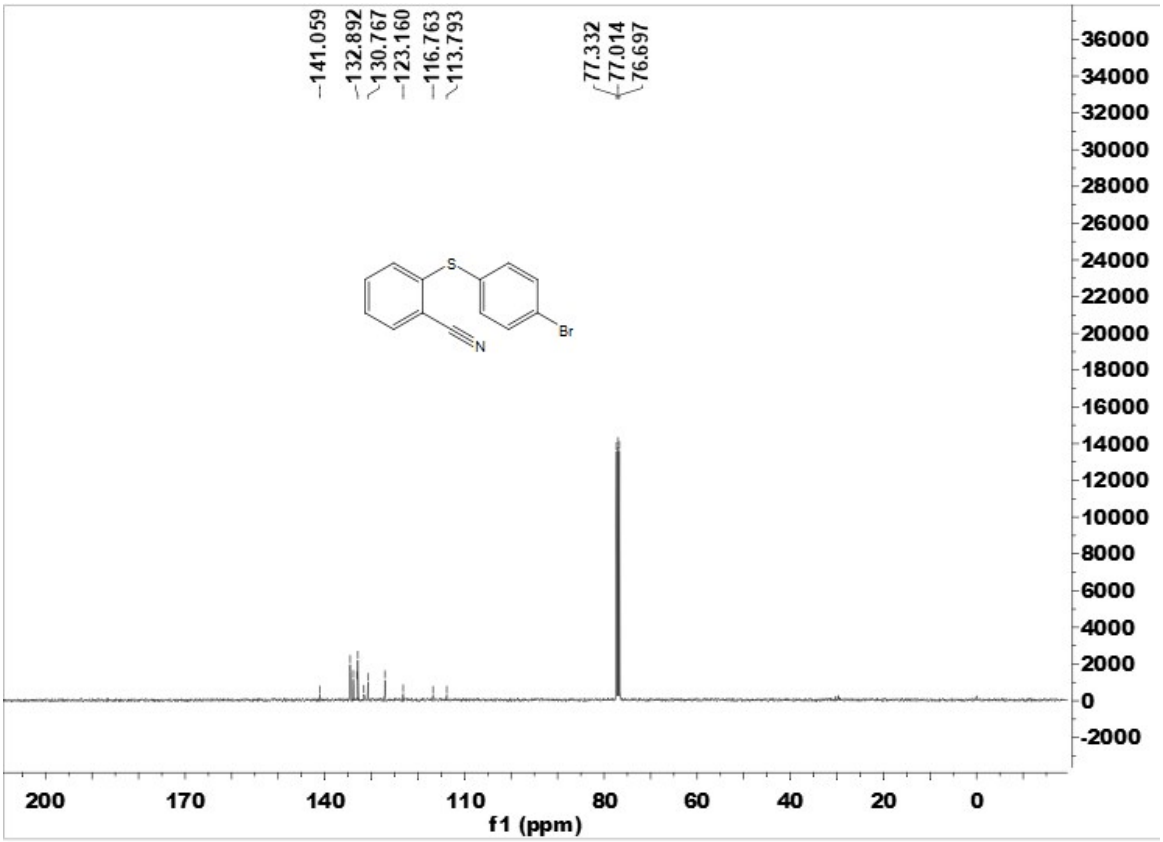

7.647
7.627
7.522
7.509
7.501
7.488
7.438
7.418
7.399
7.278
7.260
7.241
7.135
7.114
7.092
7.085
7.065
N
F
S
1.01
2.00
1.05
1.05
3.00
f1 (ppm)


164.57
162.07
142.56
136.26
136.18
133.68
133.00
129.35
126.43
117.14
116.92
112.47
77.32
77.00
76.68
N
F
S
f1 (ppm)

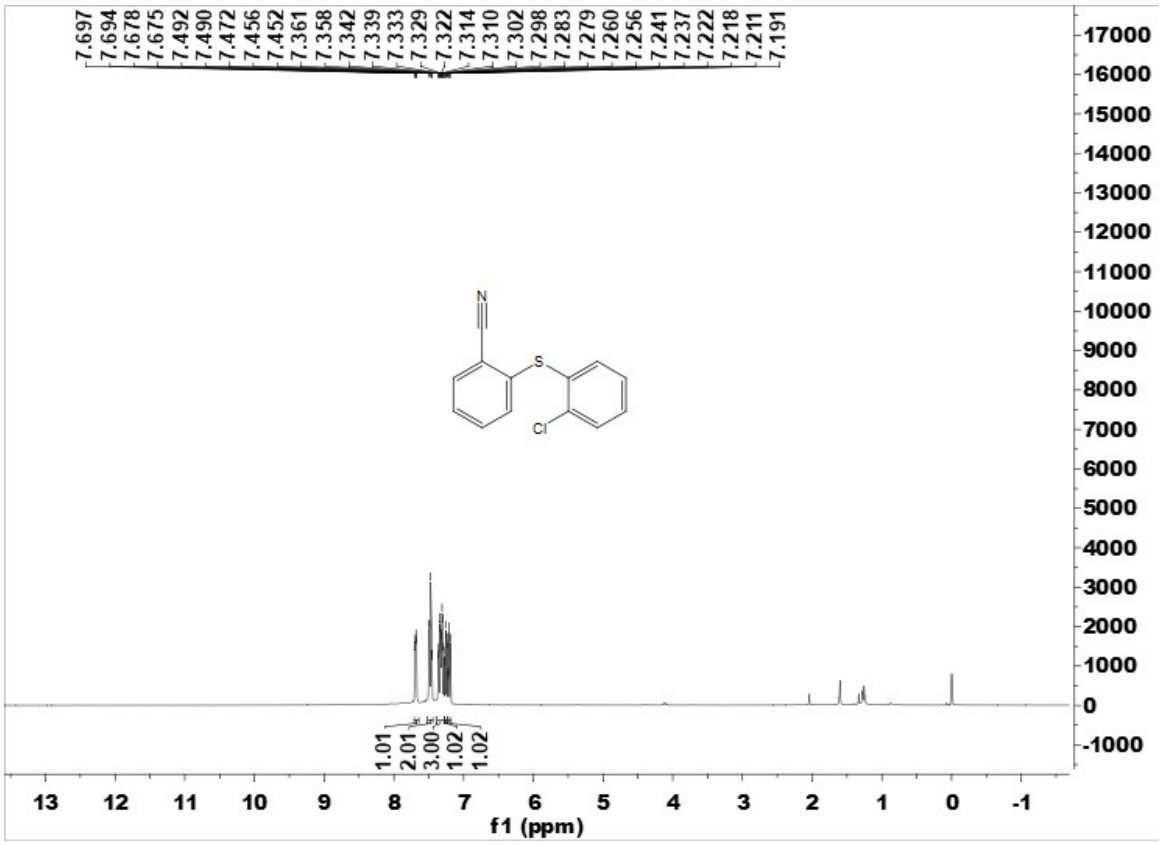


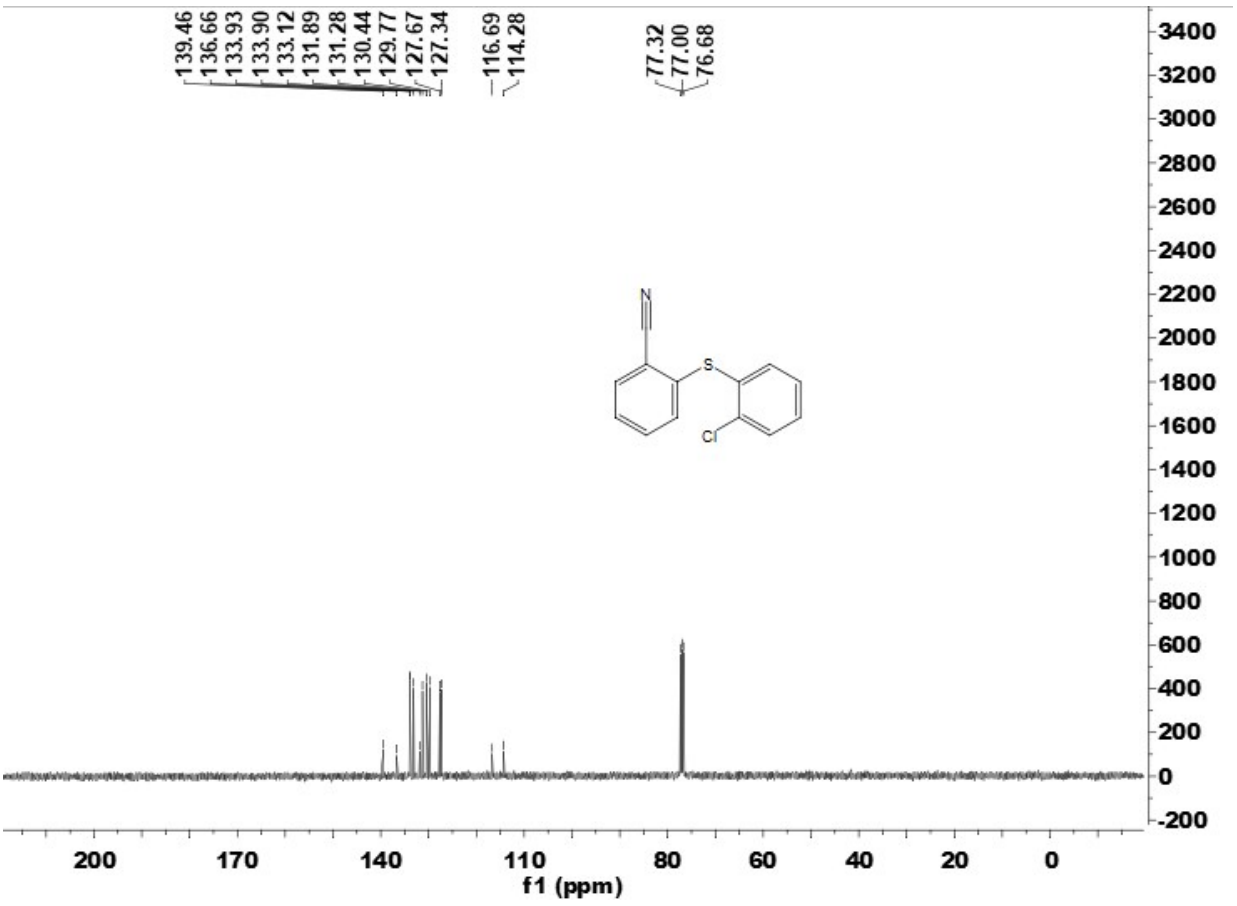
2-((4-Bromophenyl)thio)benzonitrile (3q)



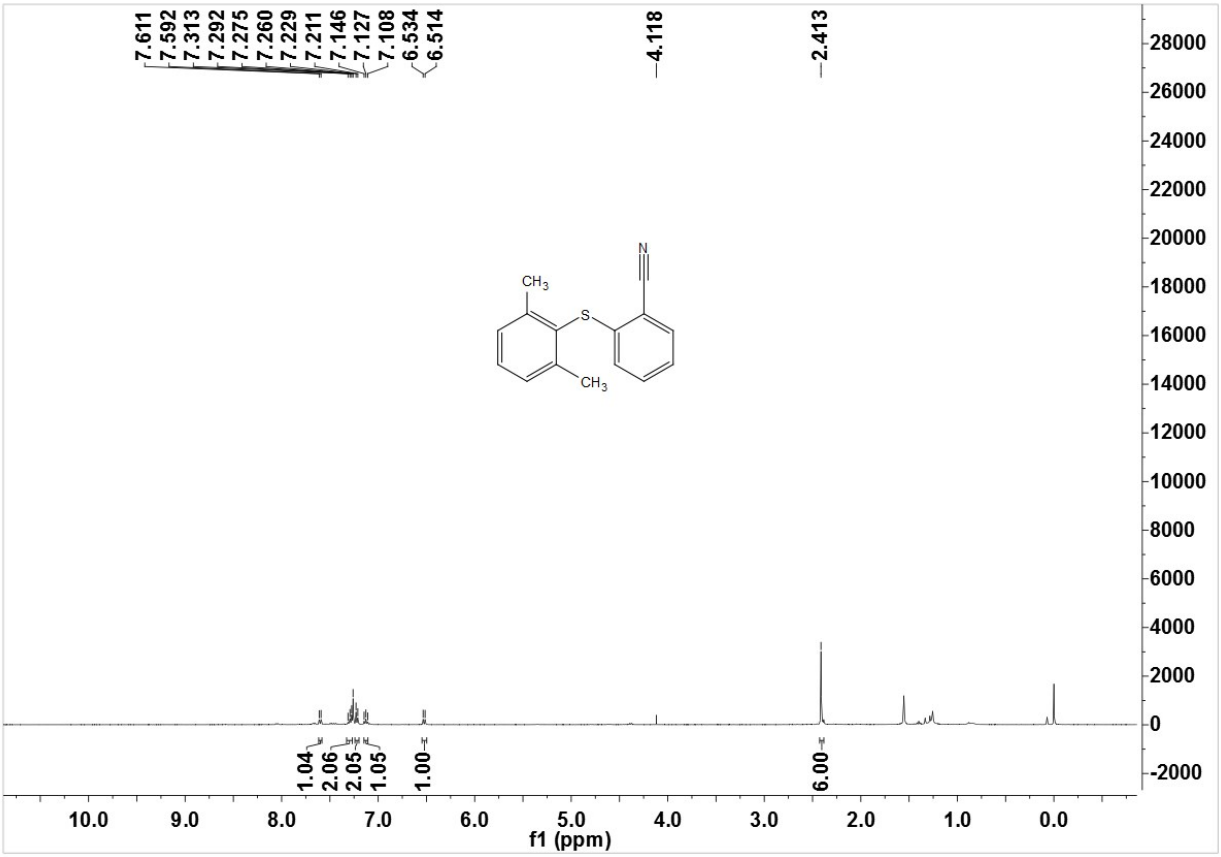


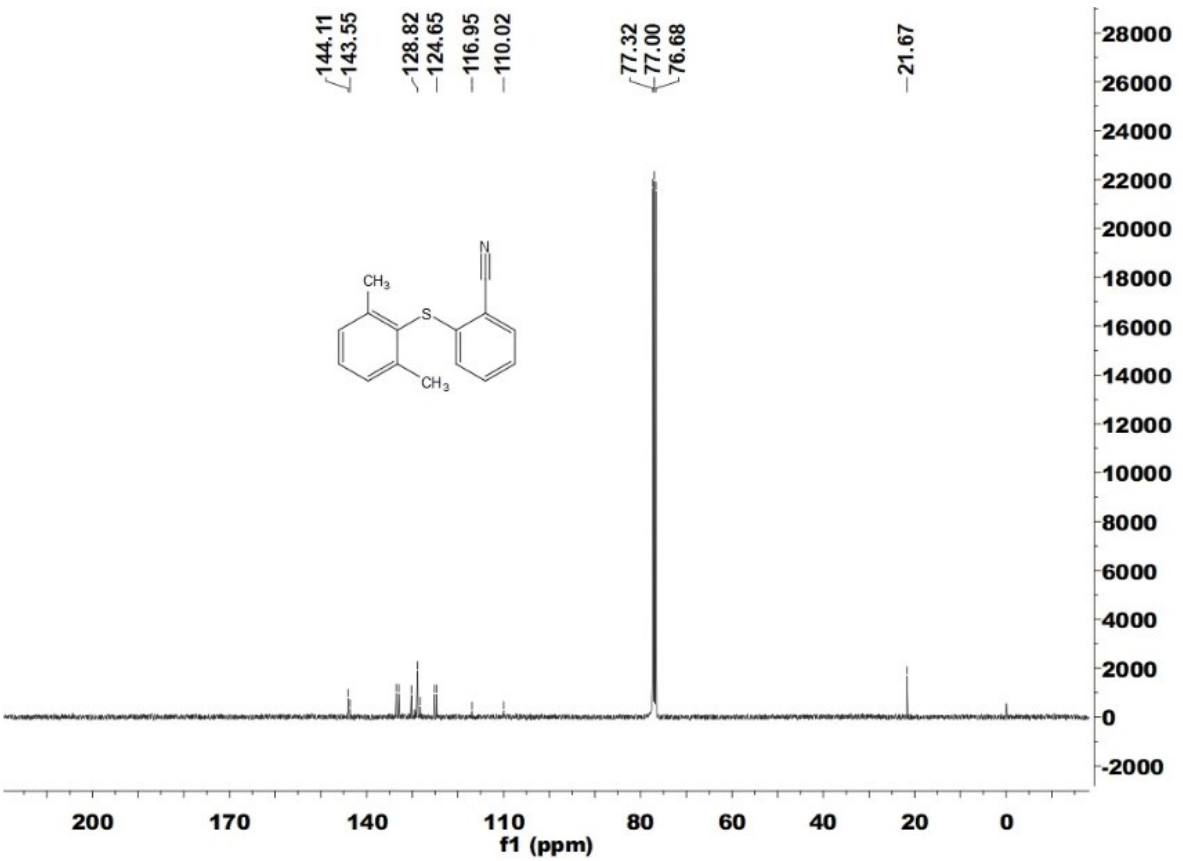
2-((2-Chlorophenyl)thio)benzonitrile (3r)



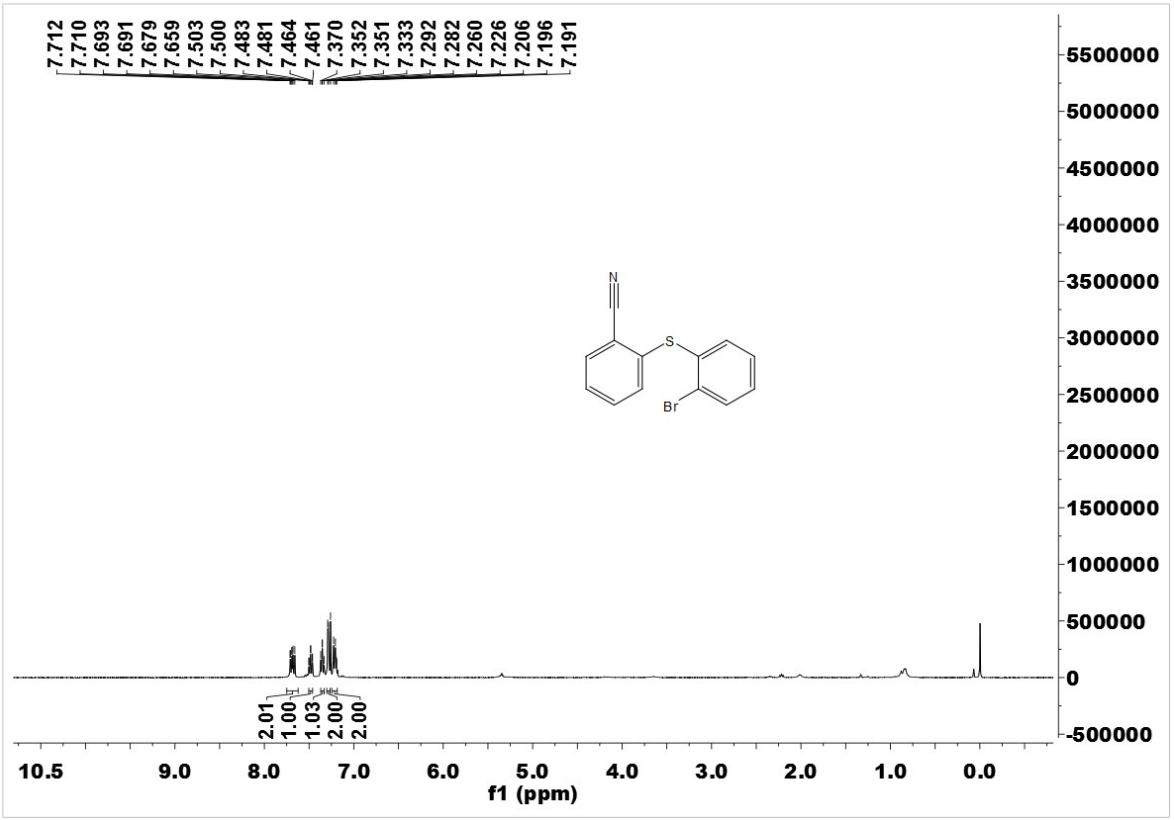


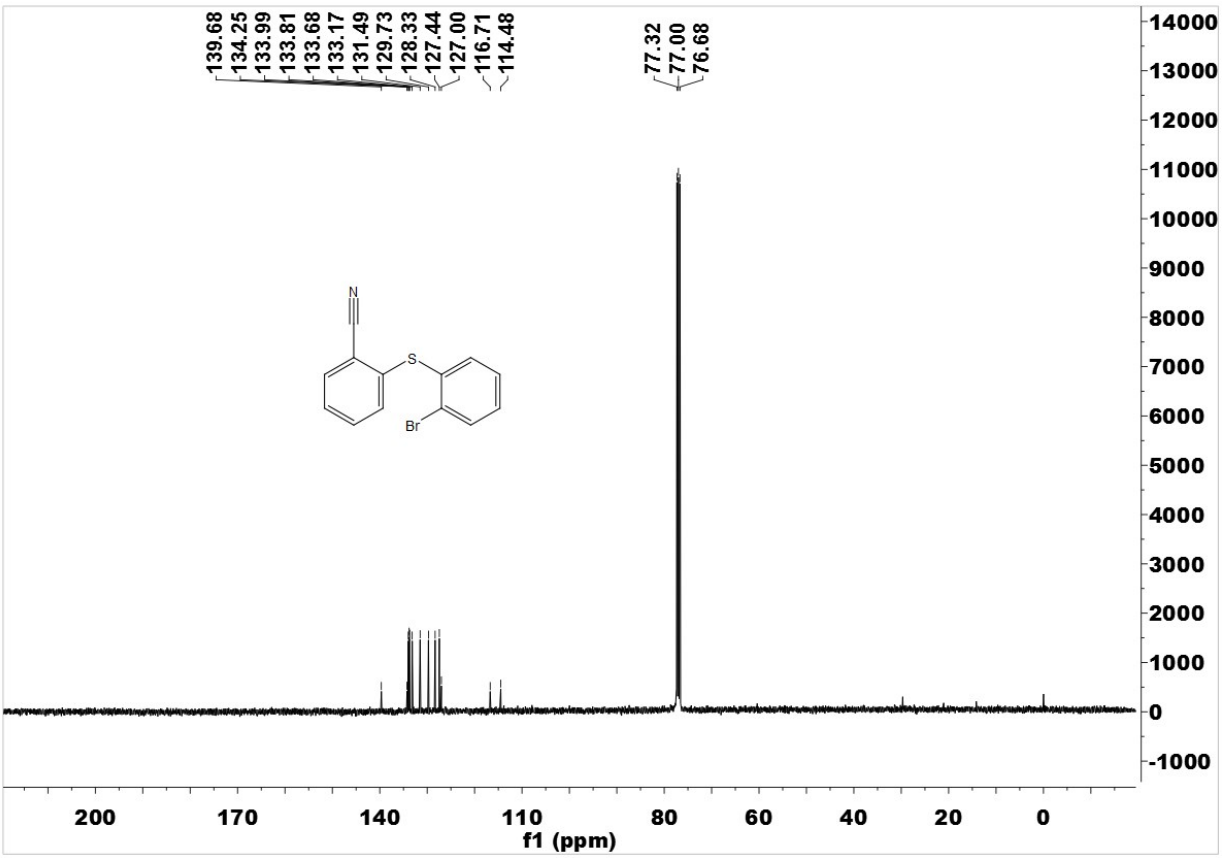
2-((2,6-Dimethylphenyl)thio)benzonitrile (3s)



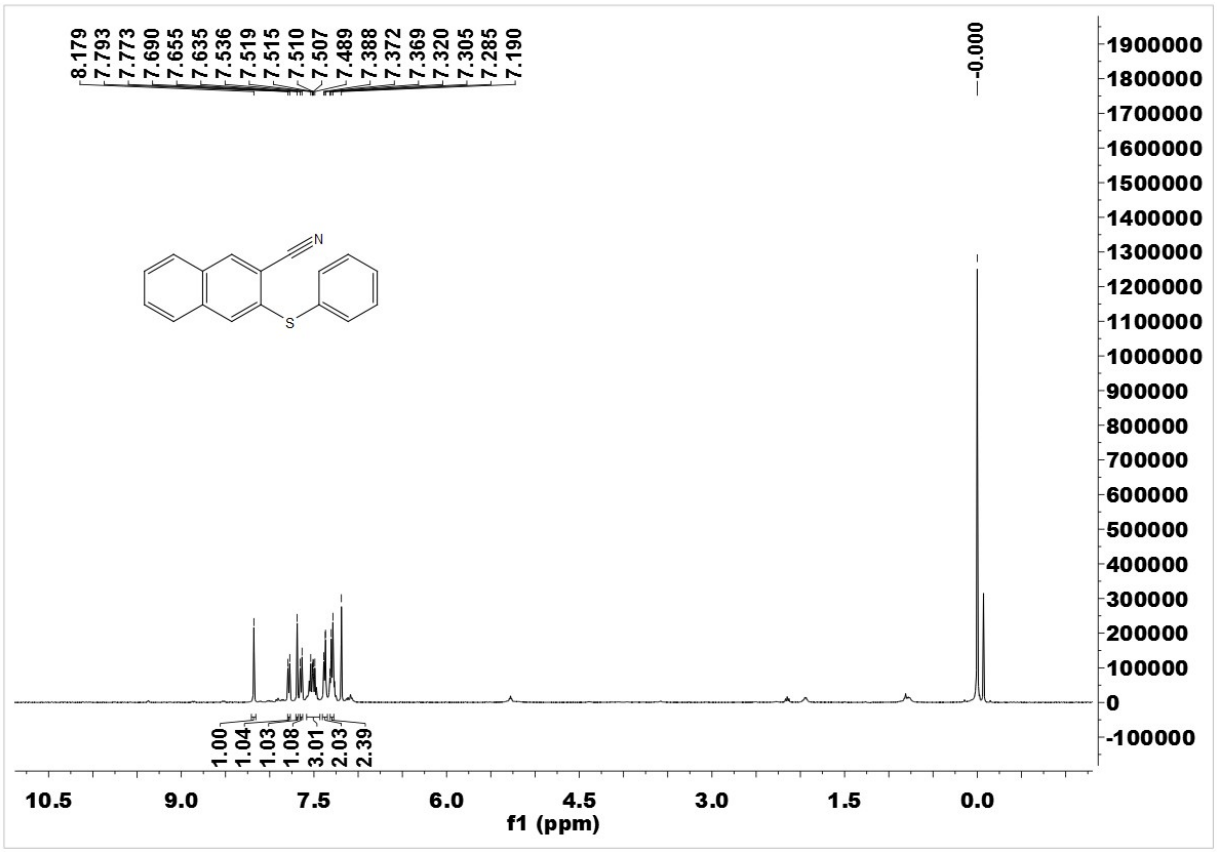


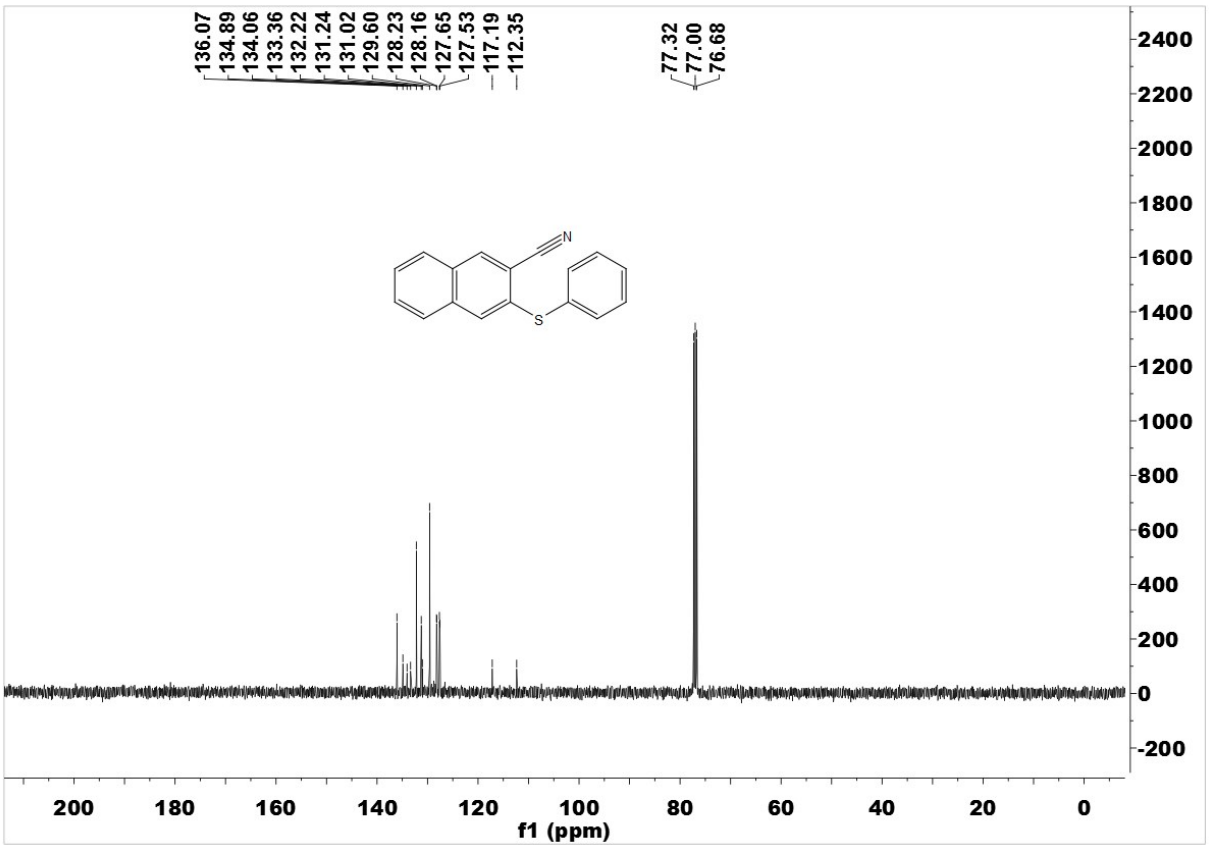
2-((2,6-Dimethylphenyl)thio)benzonitrile (3t)



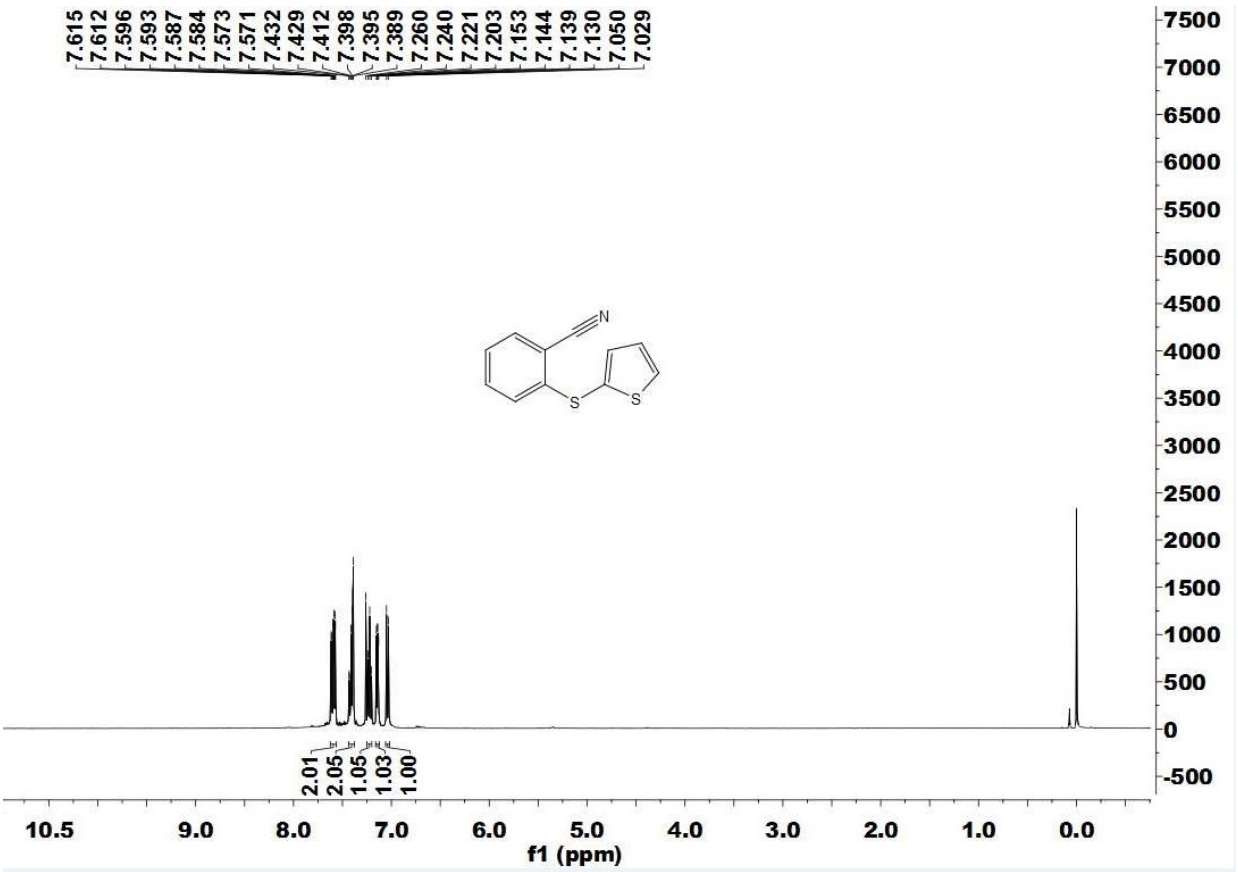


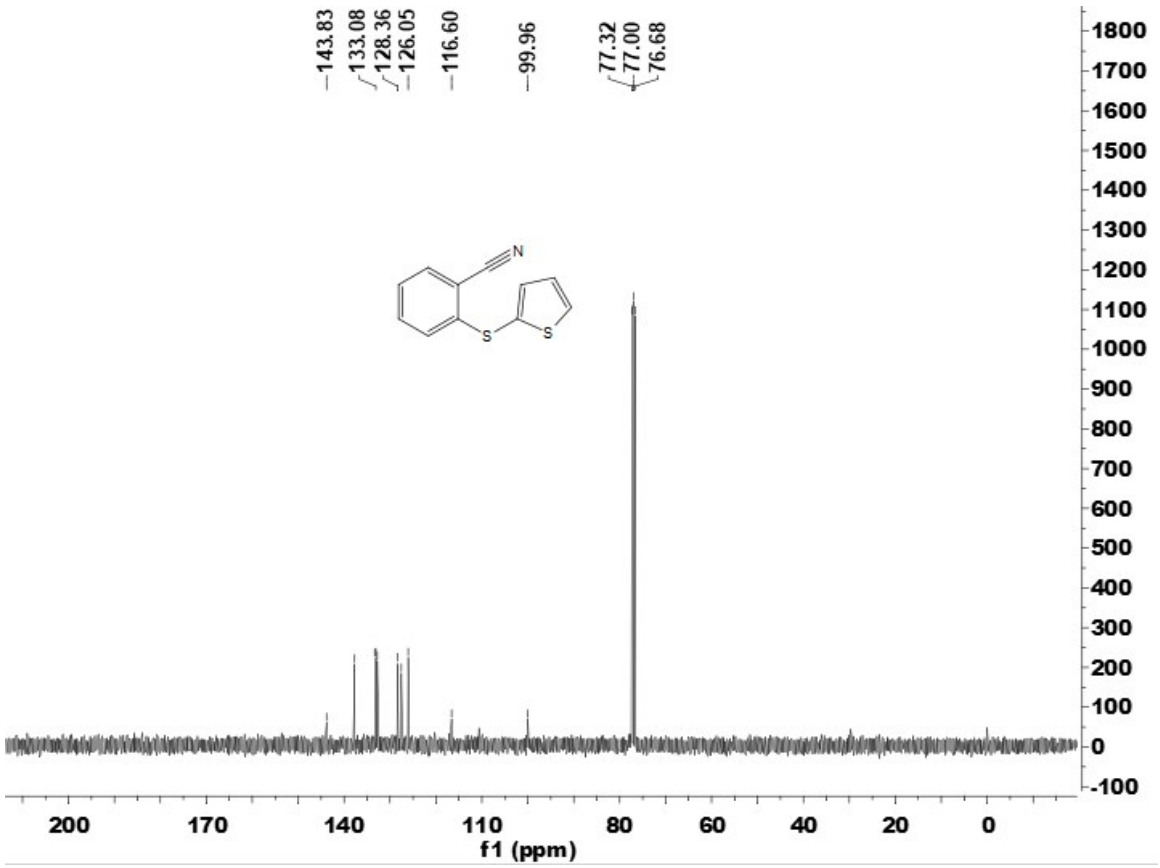
2-(Naphthalen-2-ylthio)benzonitrile (3u)



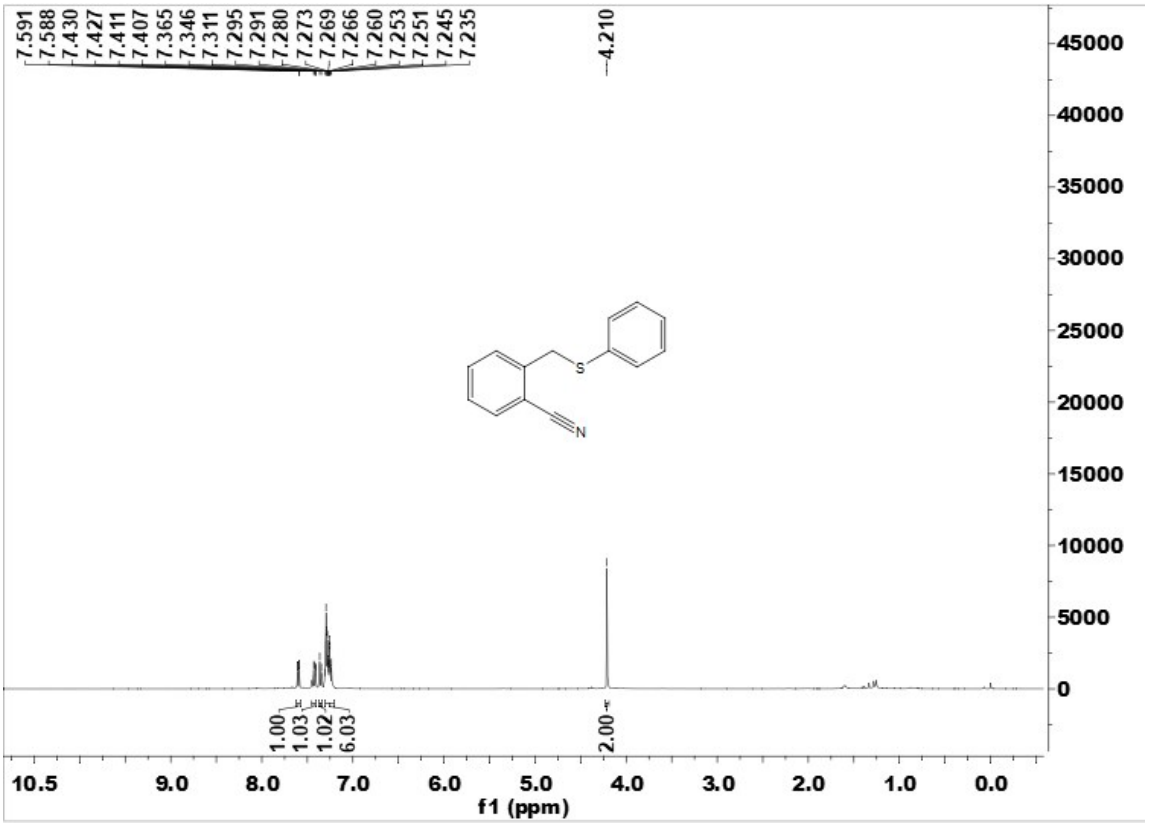


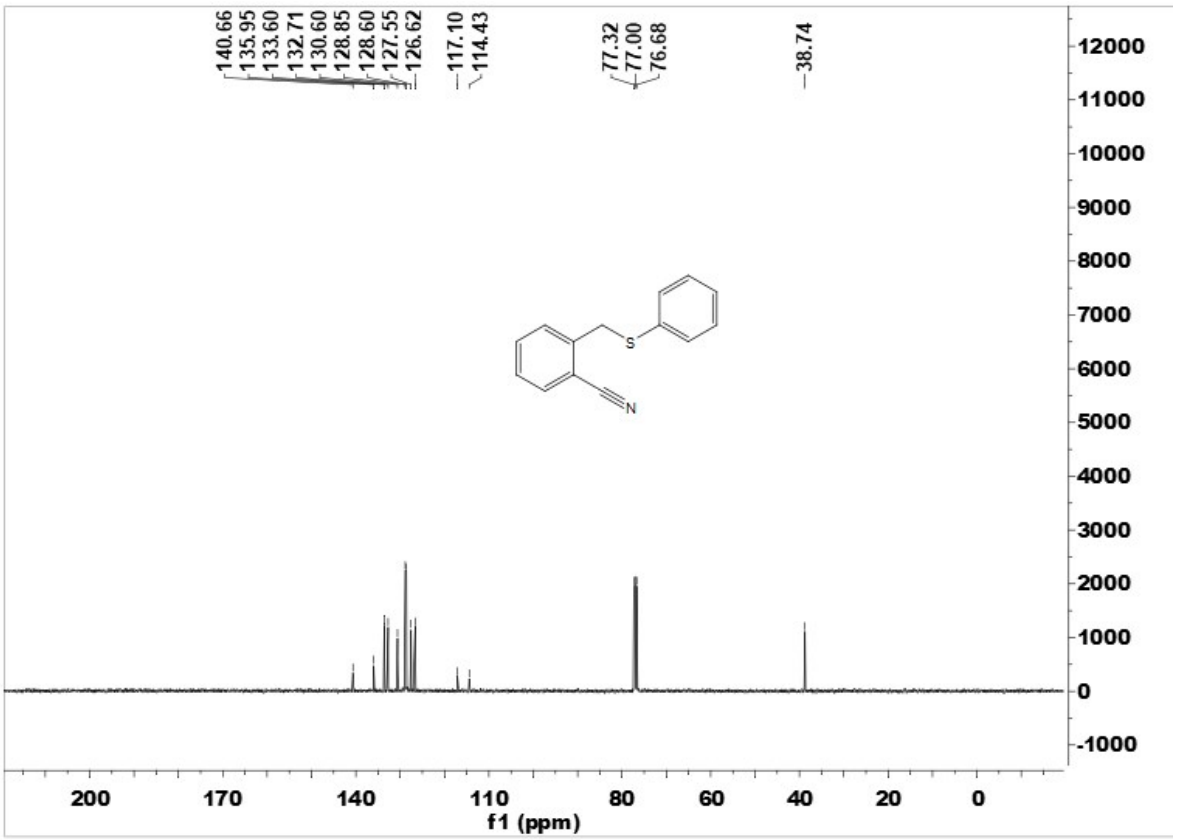
2-(Thiophen-2-ylthio)benzonitrile (3v)



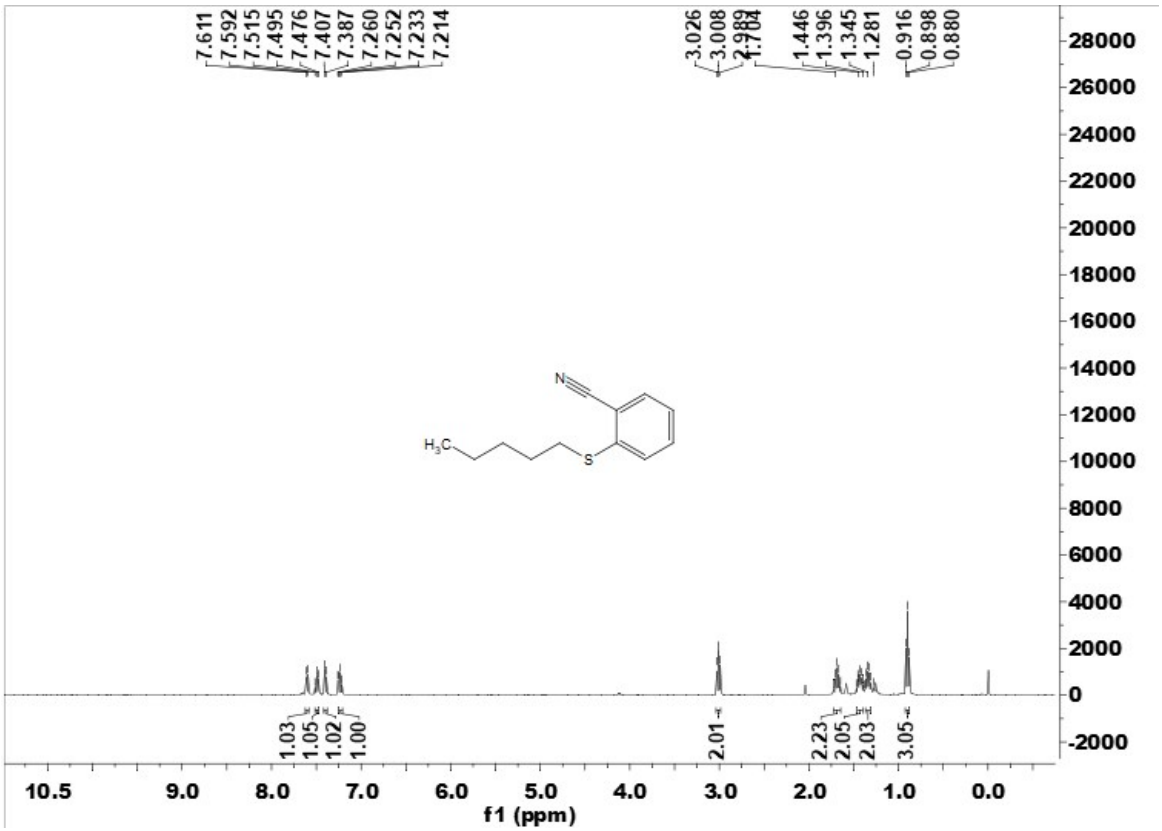


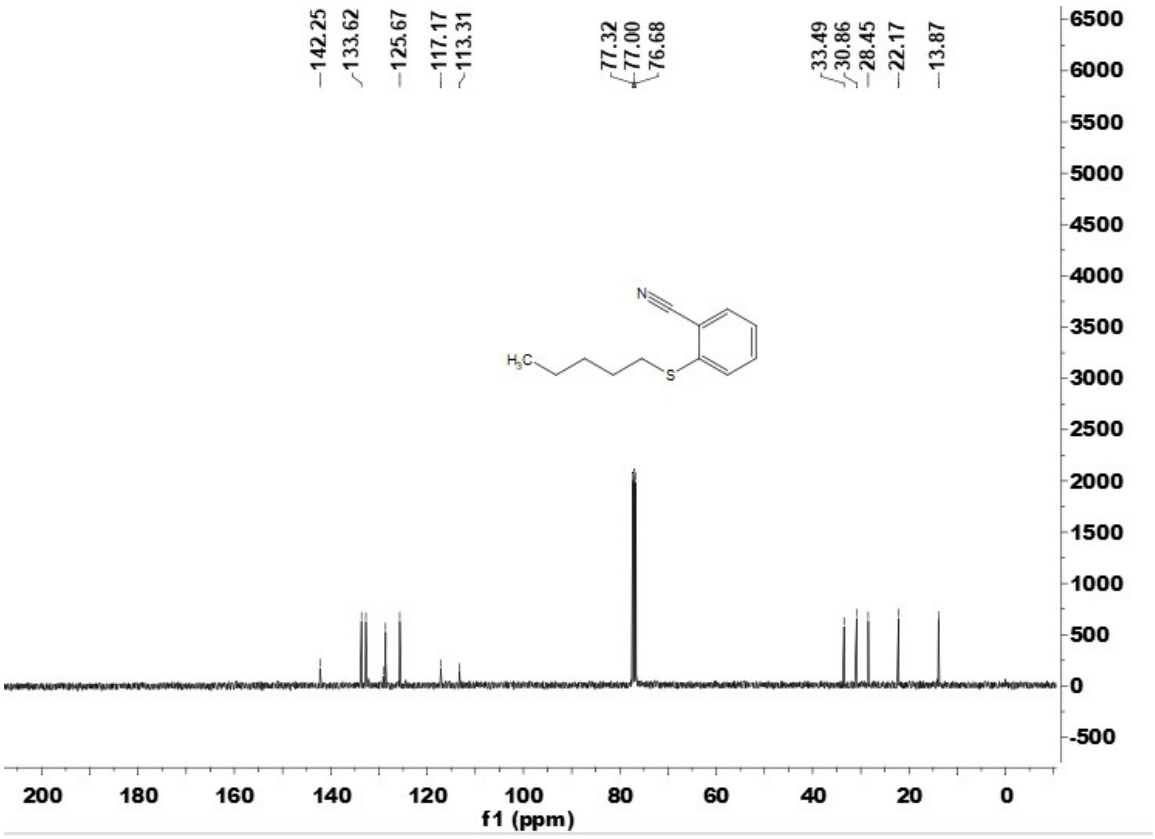
2-((Phenylthio)methyl)benzonitrile (3w)



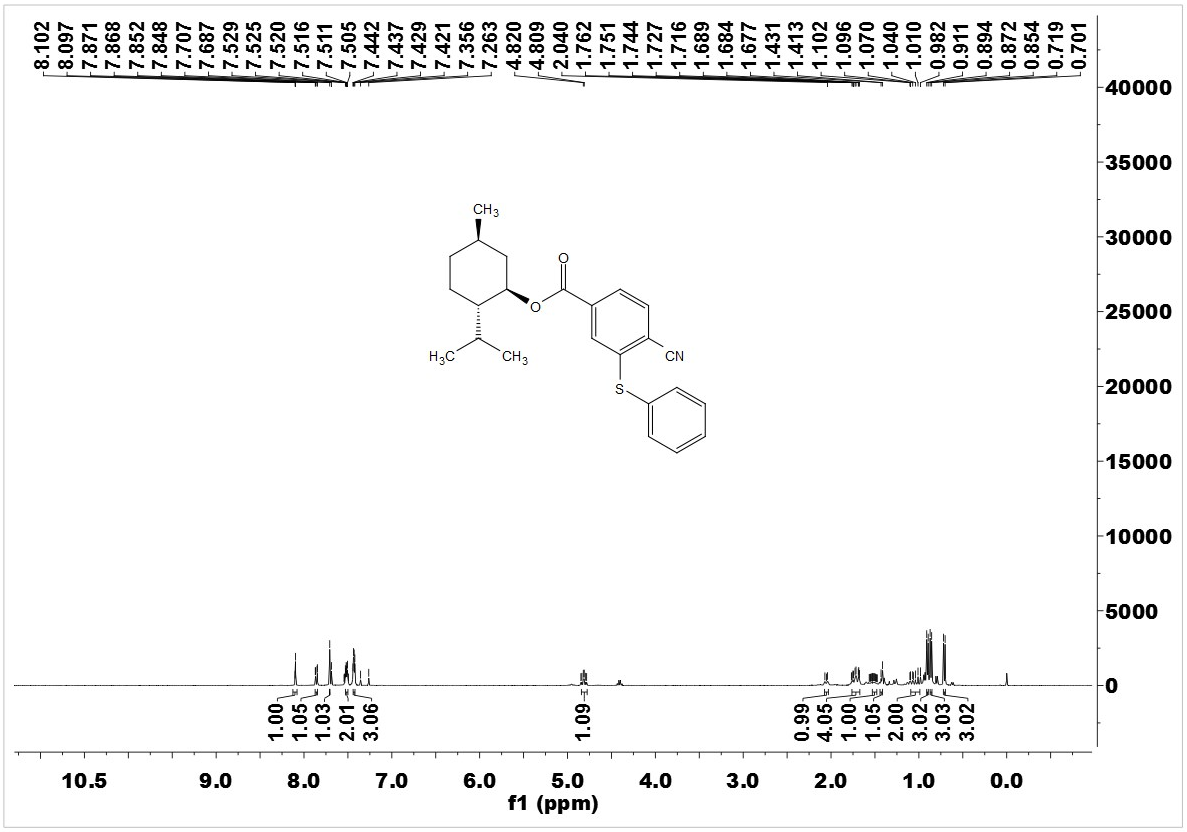


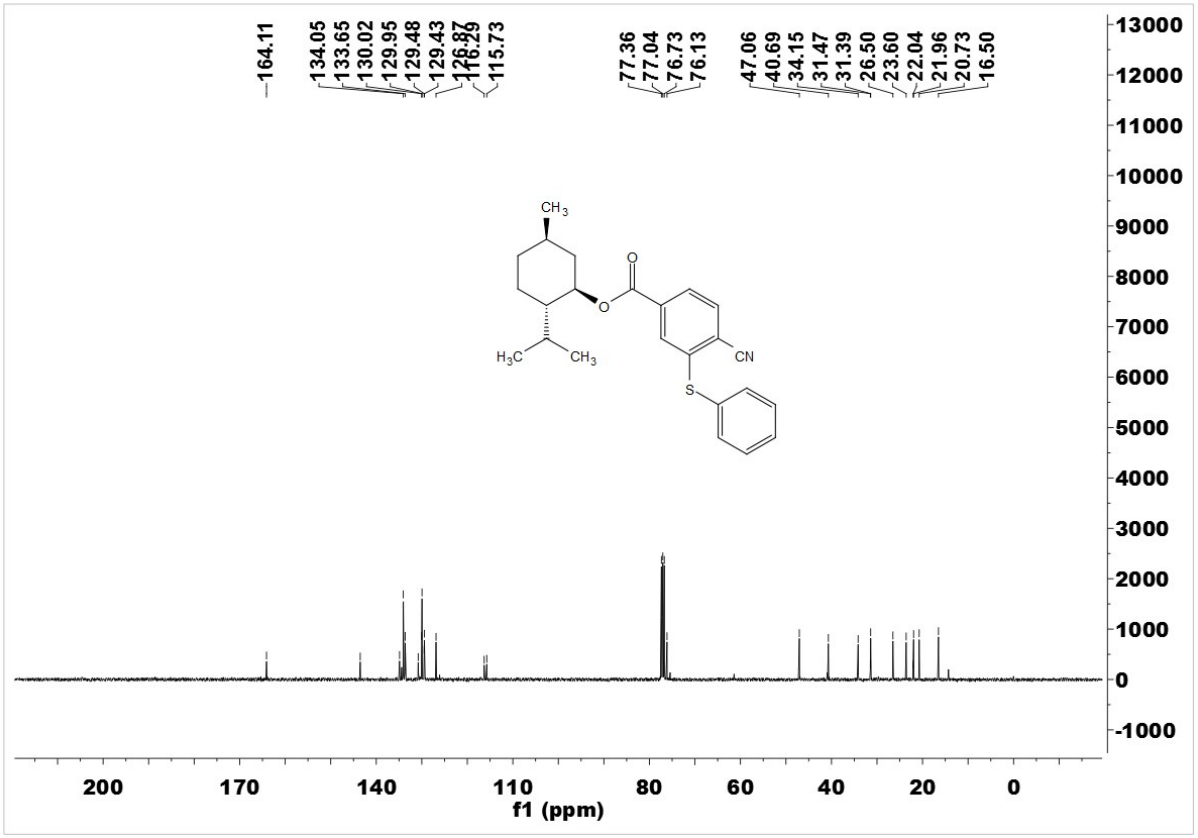
2-(Pentylthio)benzonitrile (3x)



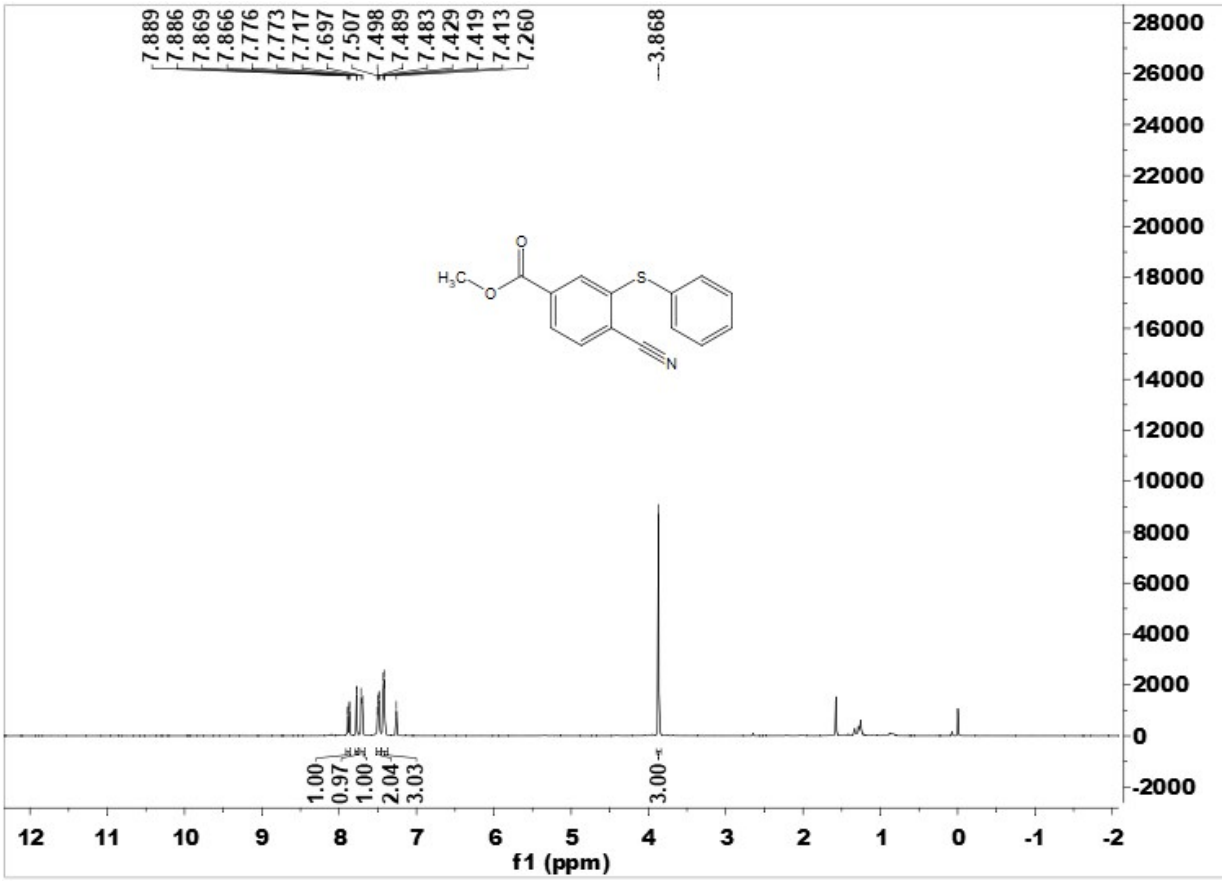


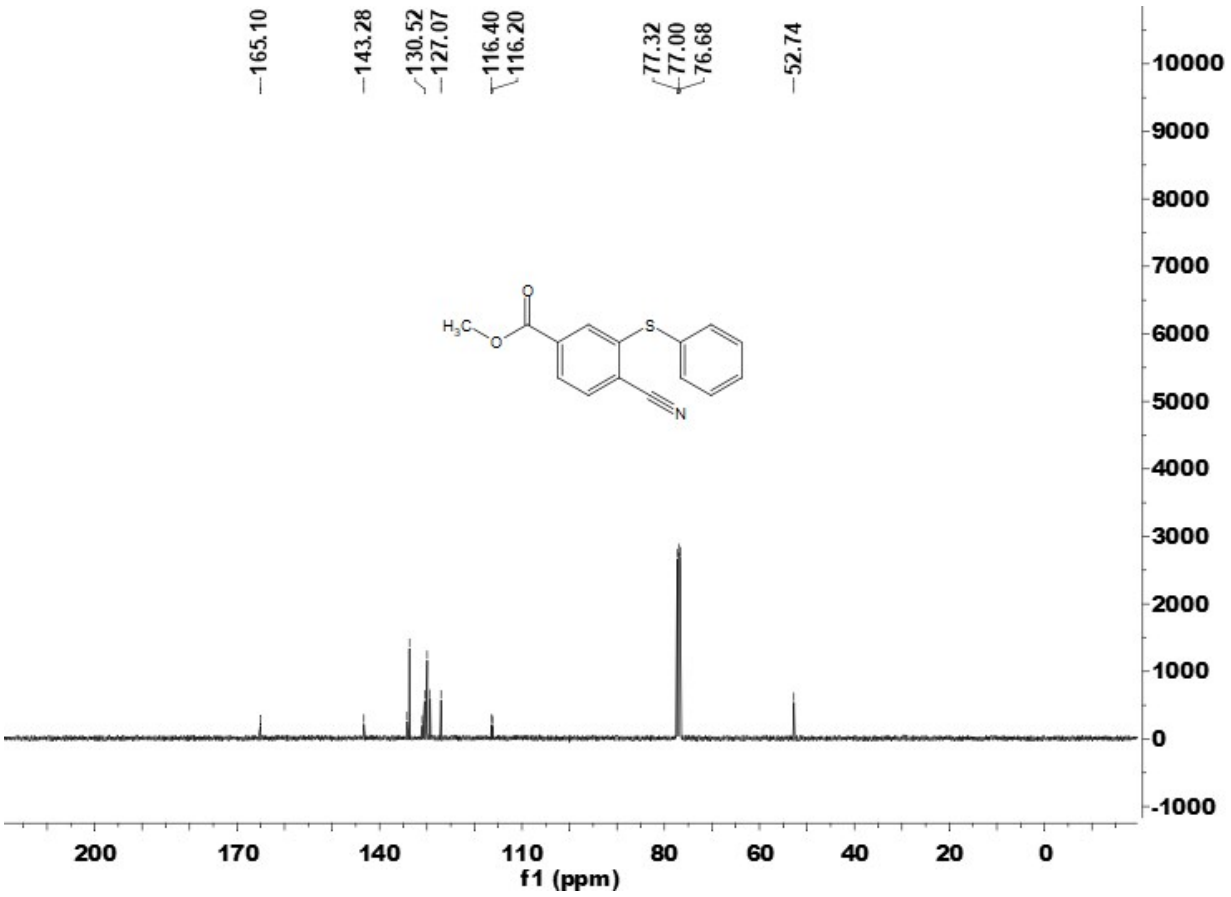
(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 4-cyano-3-(phenylthio)benzoate (3y)



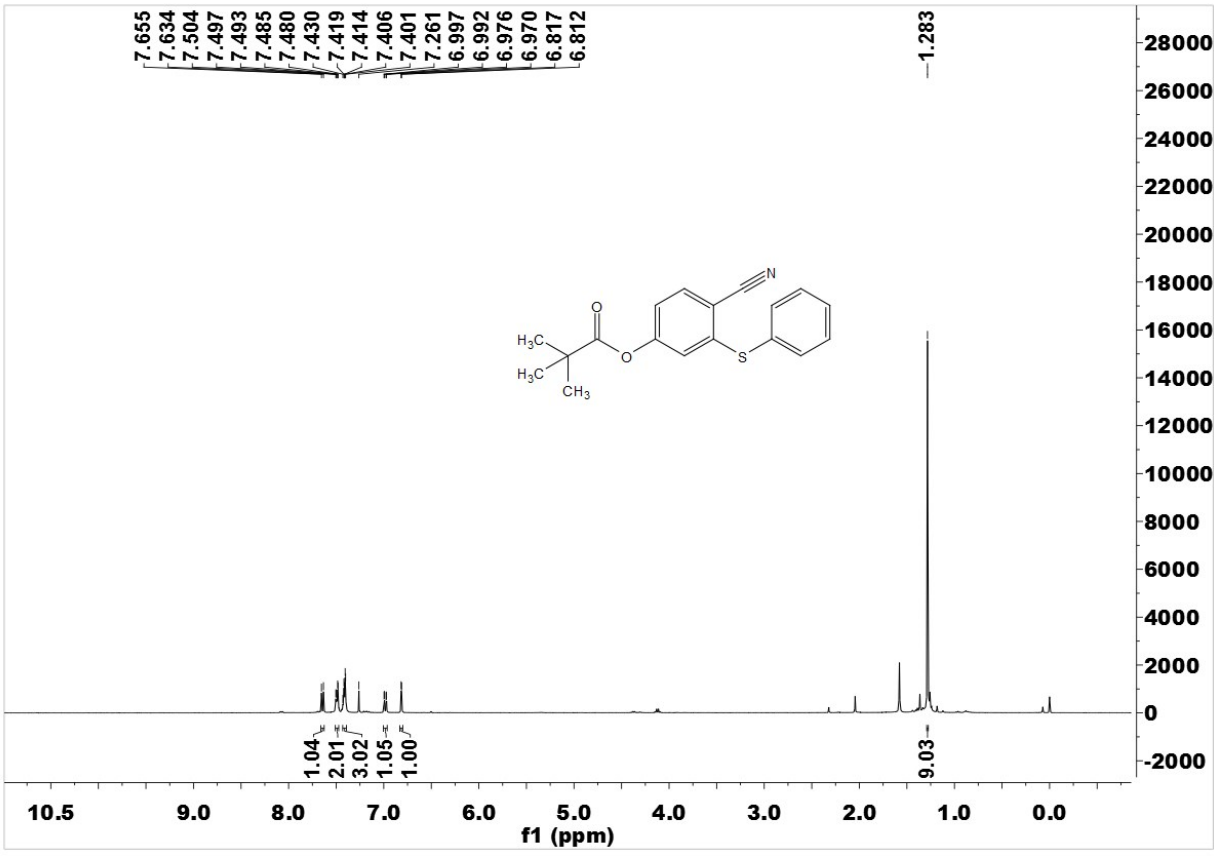


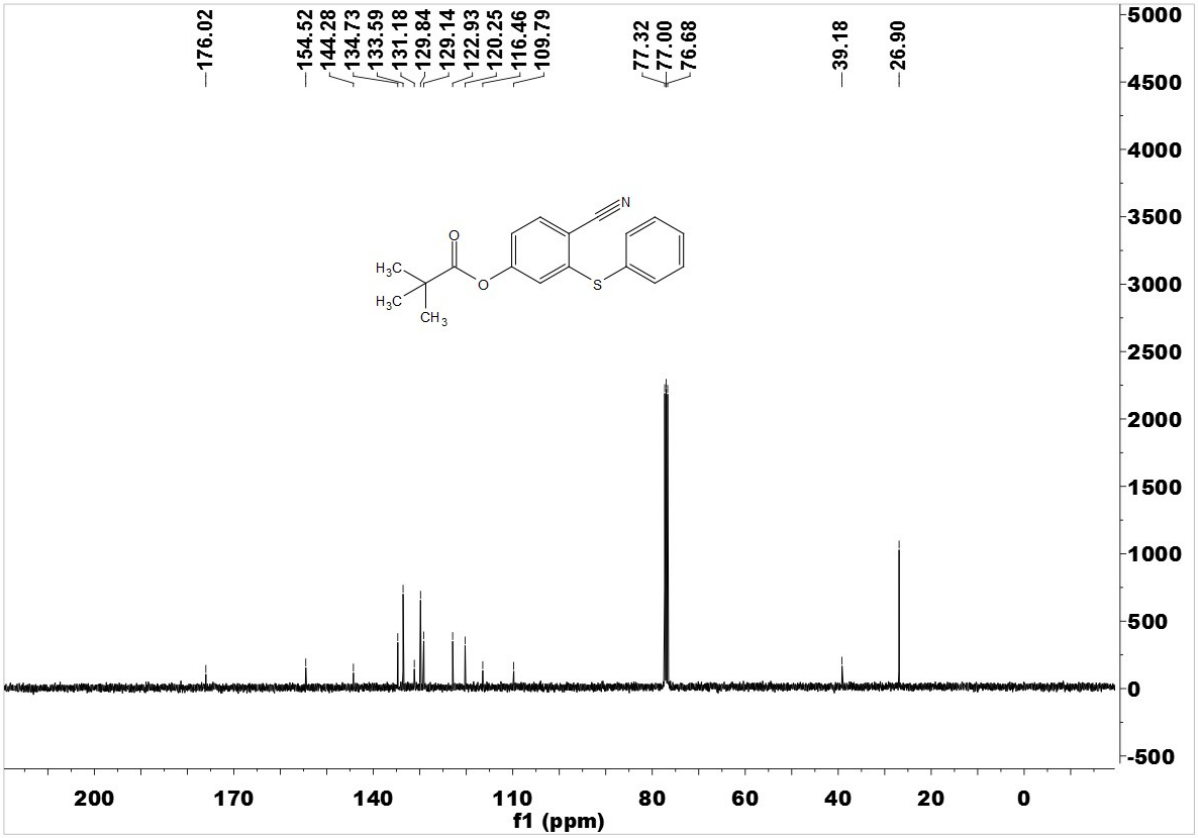
Methyl 4-cyano-3-(phenylthio)benzoate (3z)



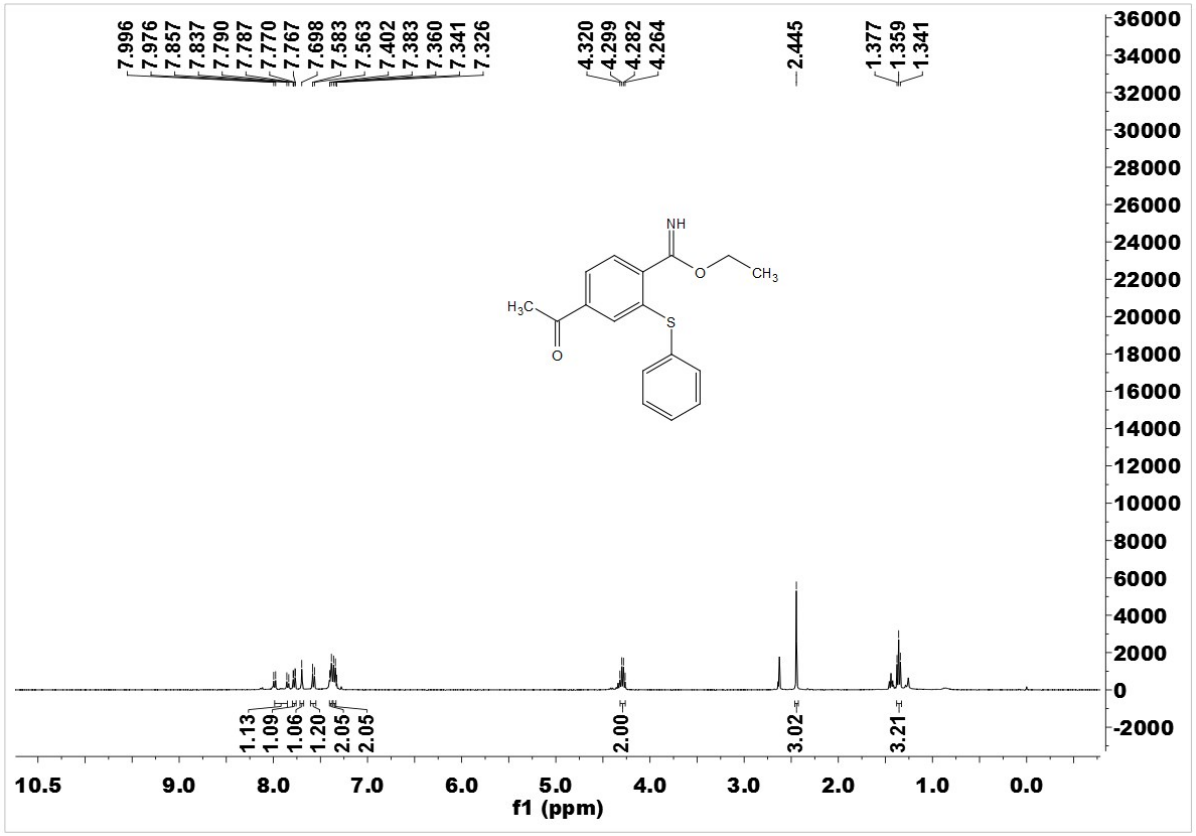


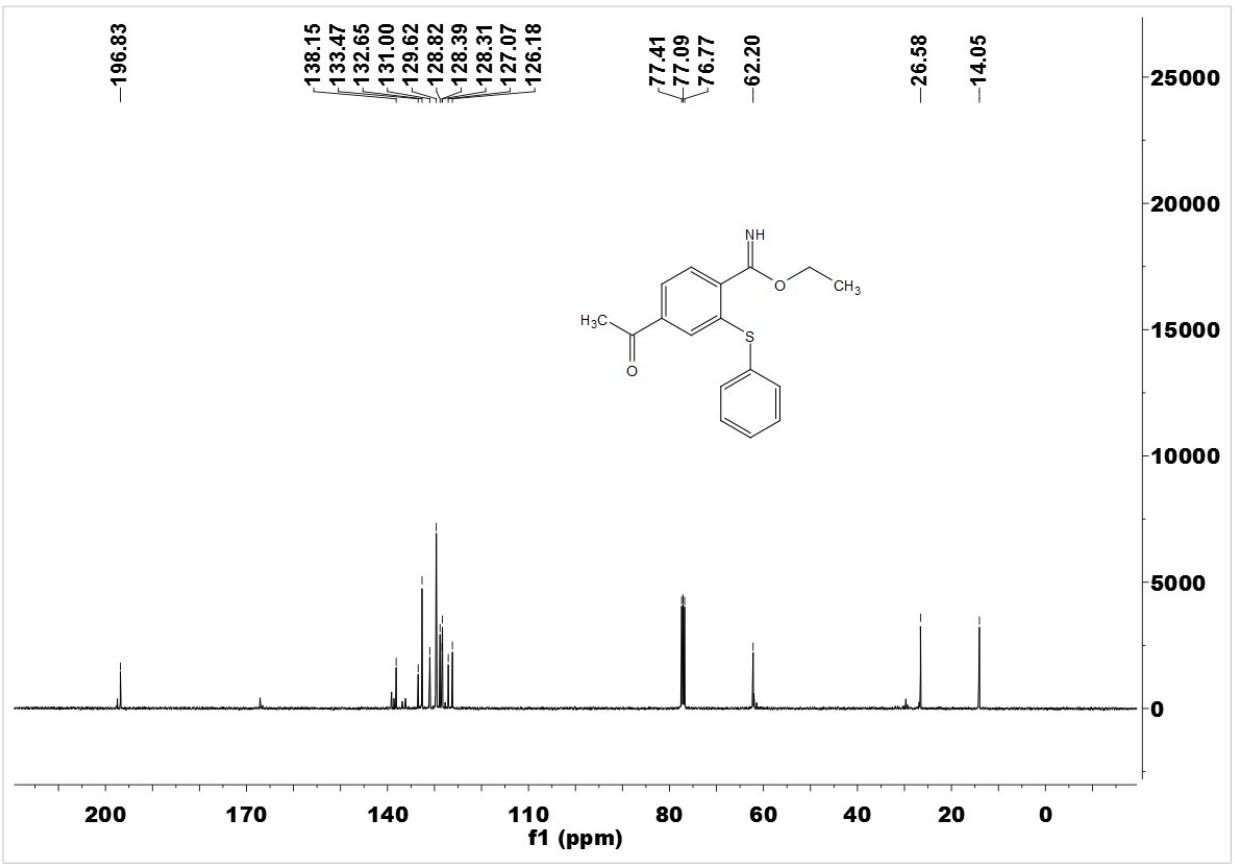
4-Cyano-3-(phenylthio)phenyl pivalate (3za)



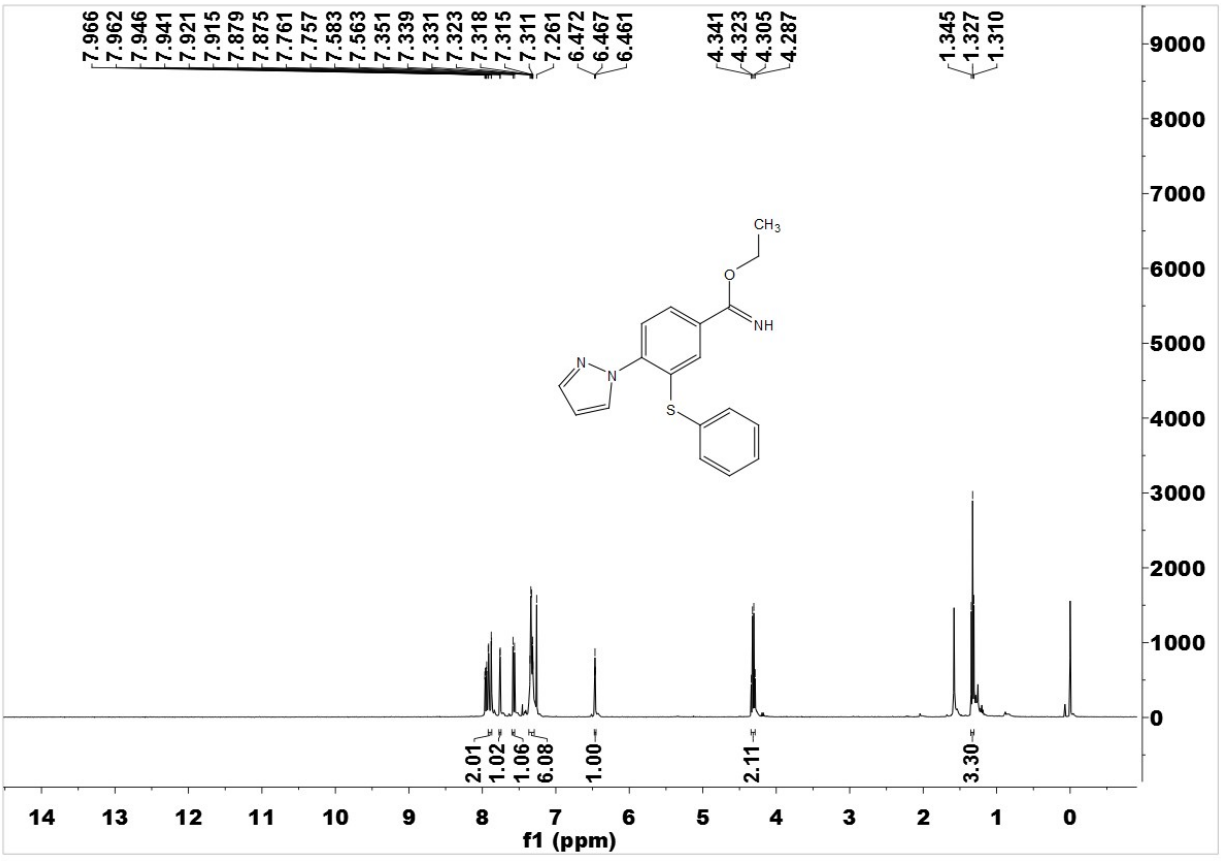


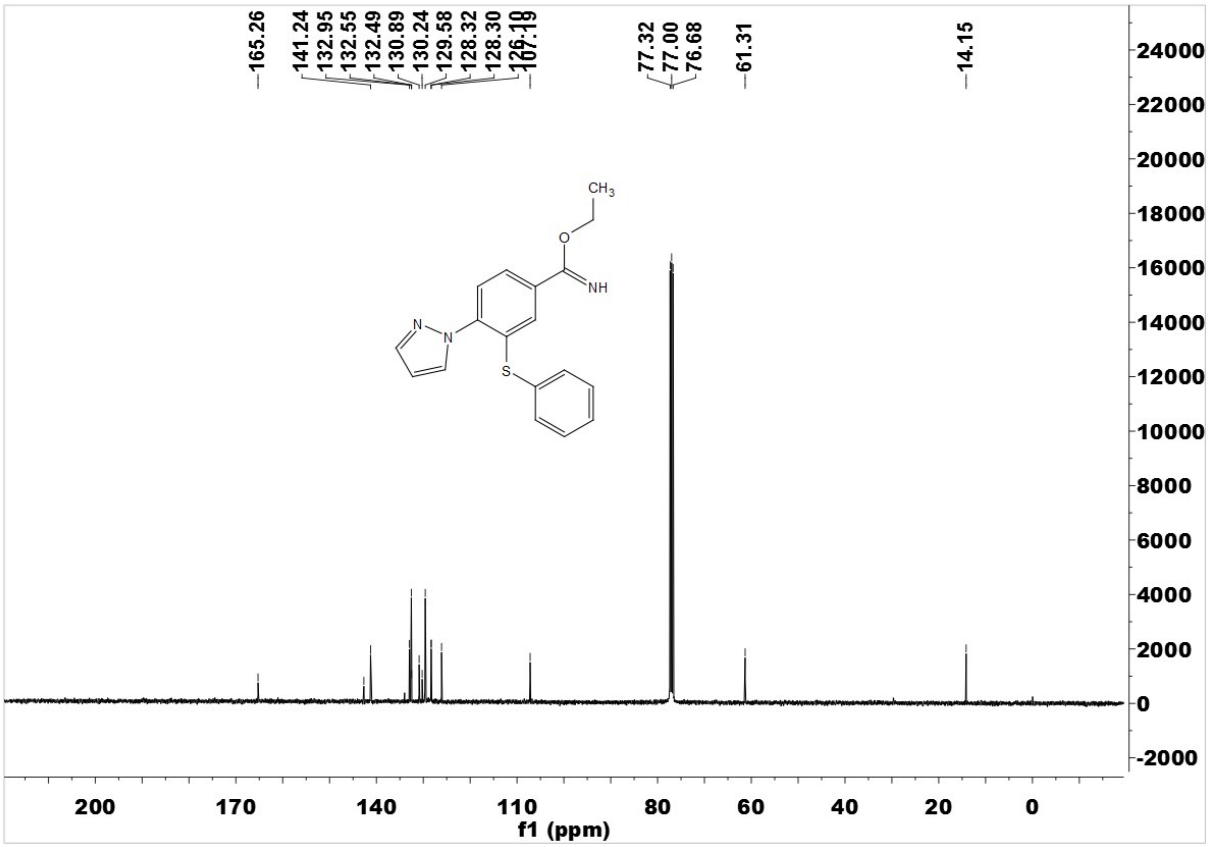
Ethyl 4-acetyl-2-(phenylthio)benzimidate (4k)



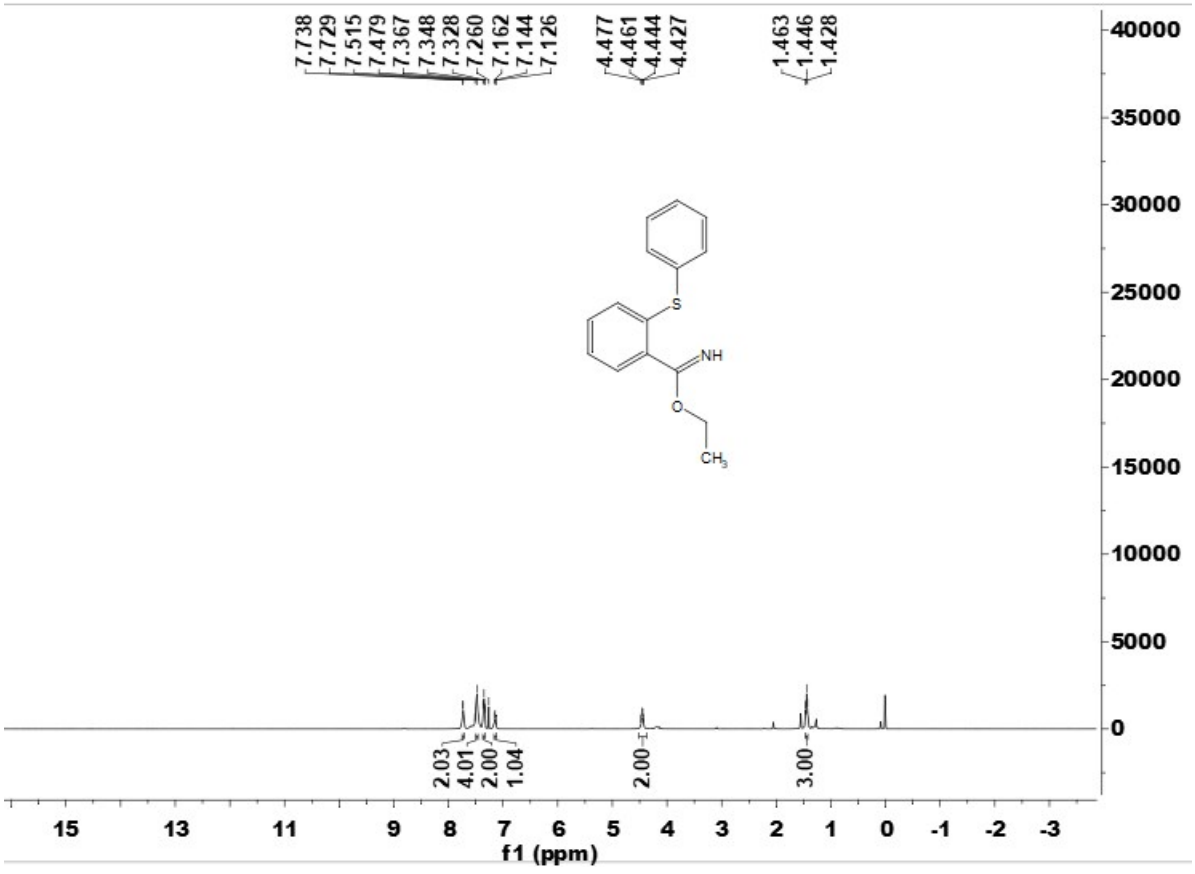


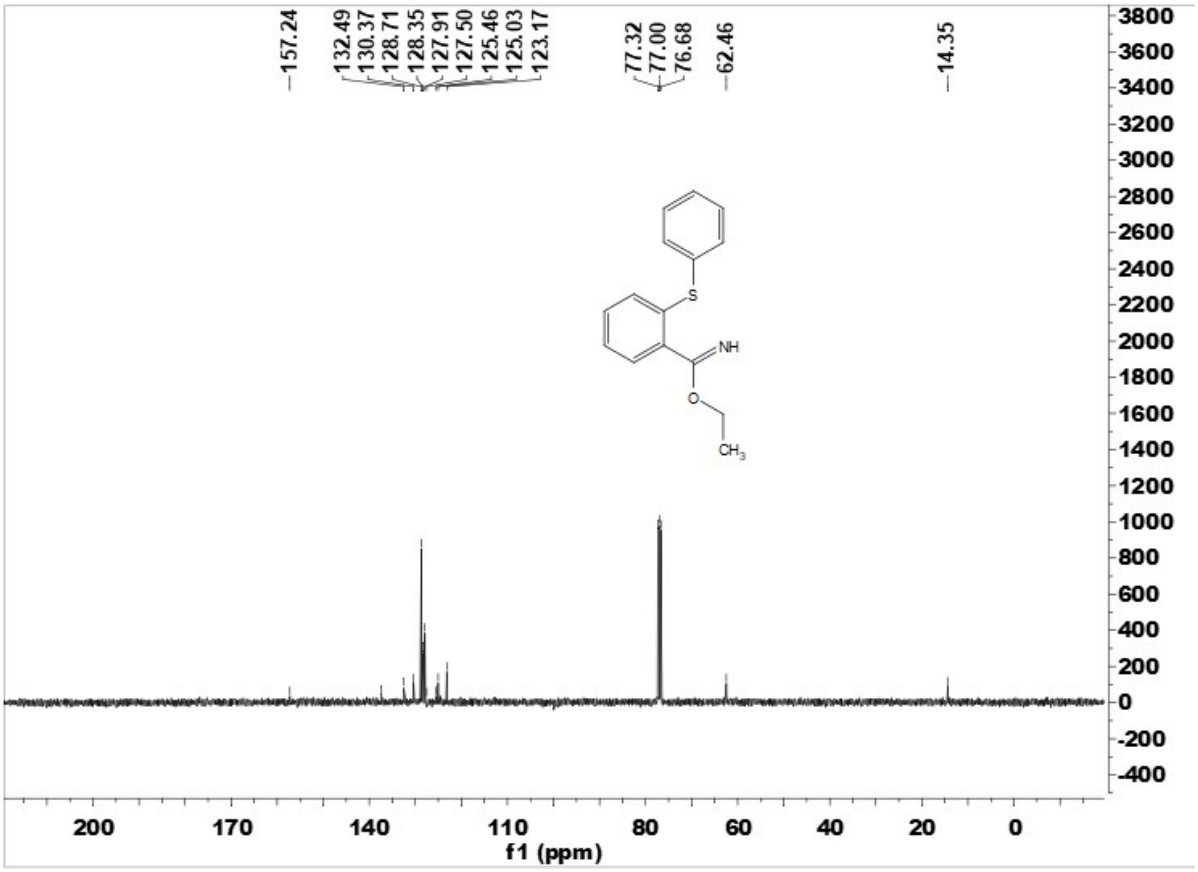
Ethyl 3-(phenylthio)-4-(1*H*-pyrazol-1-yl)benzimidate (4l)



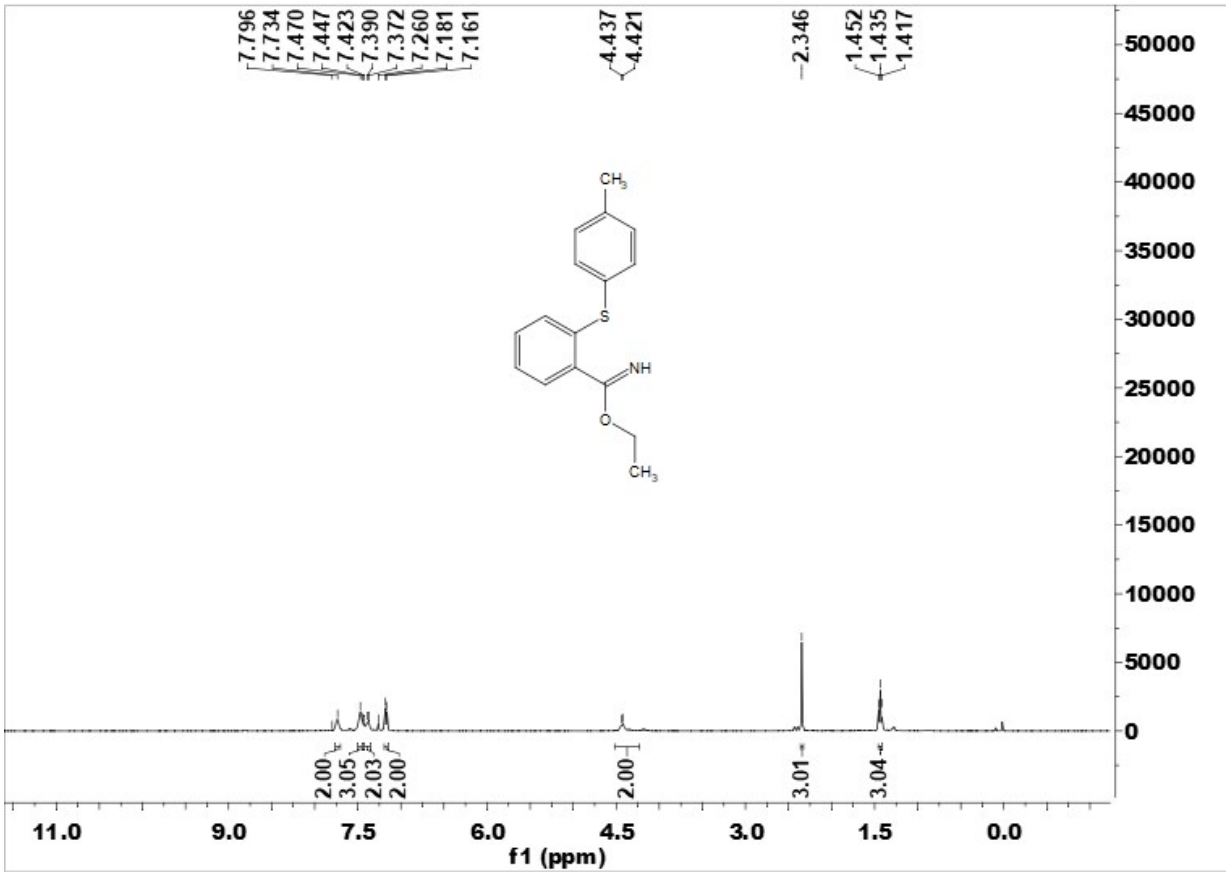


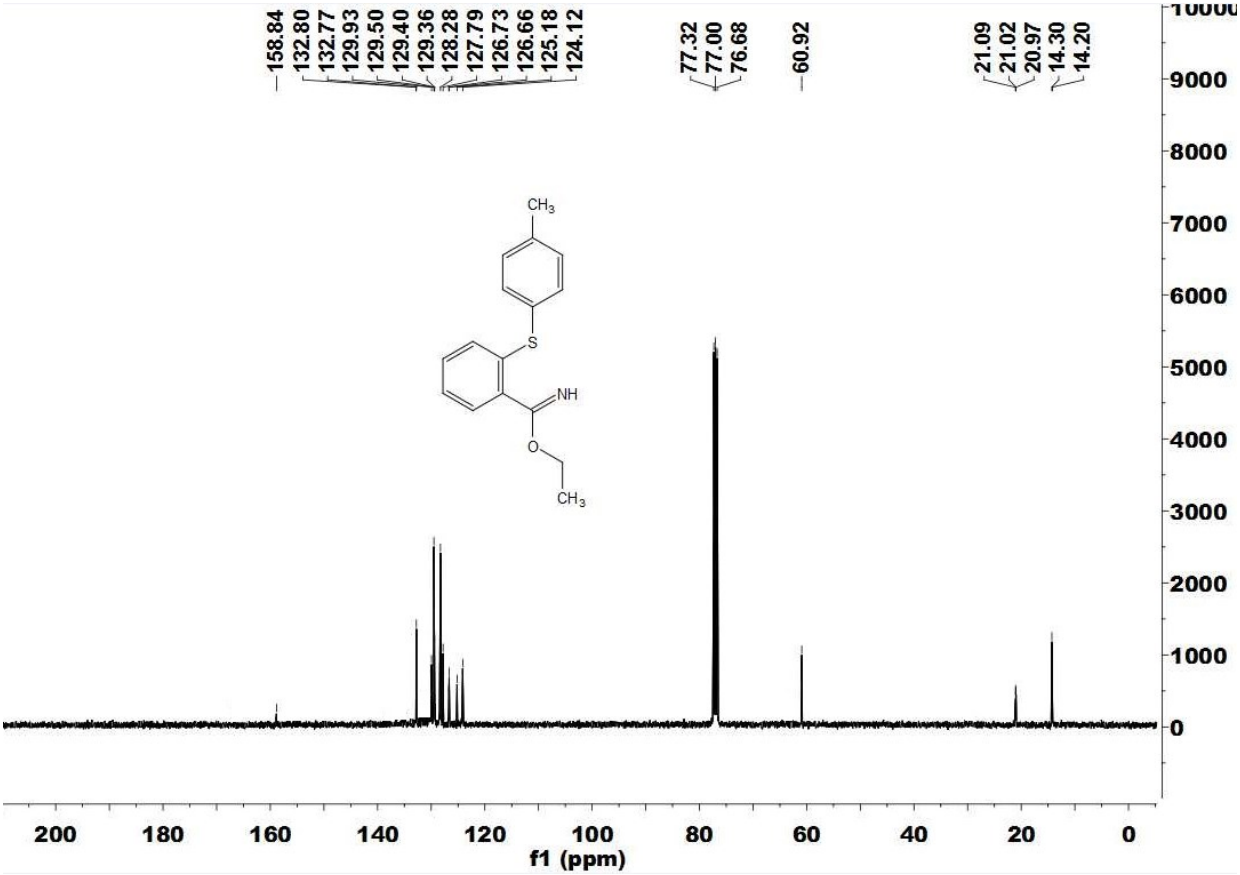
Ethyl 2-(phenylthio)benzimidate (4a)



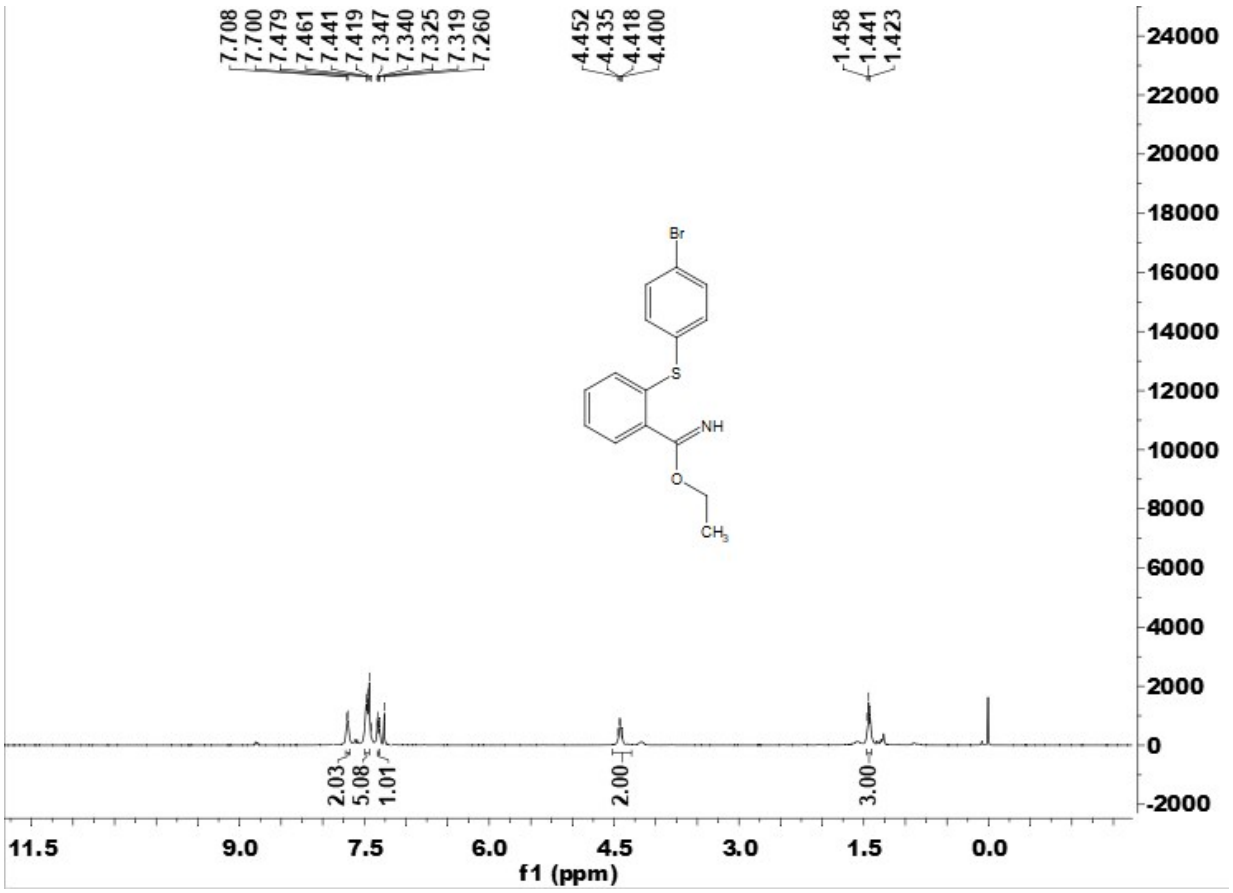


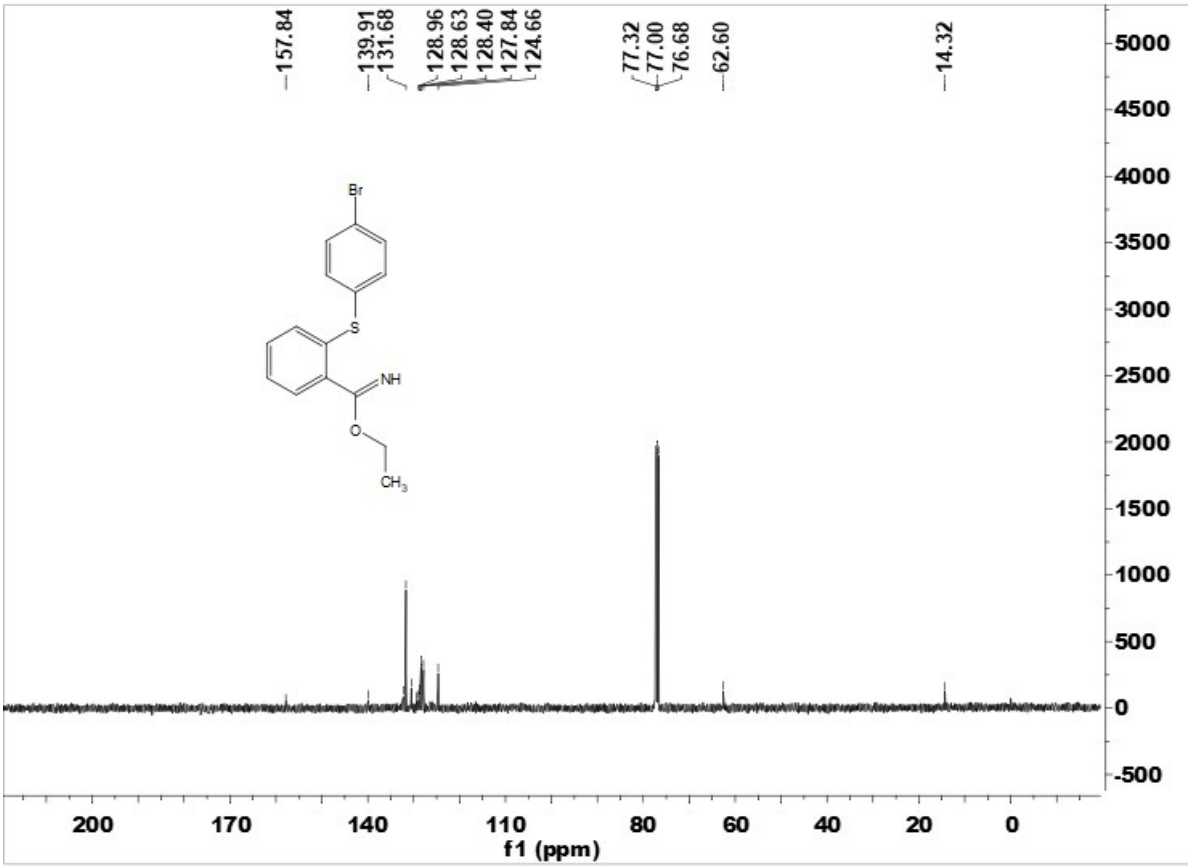
Ethyl 2-(*p*-tolylthio)benzimidate (4b)



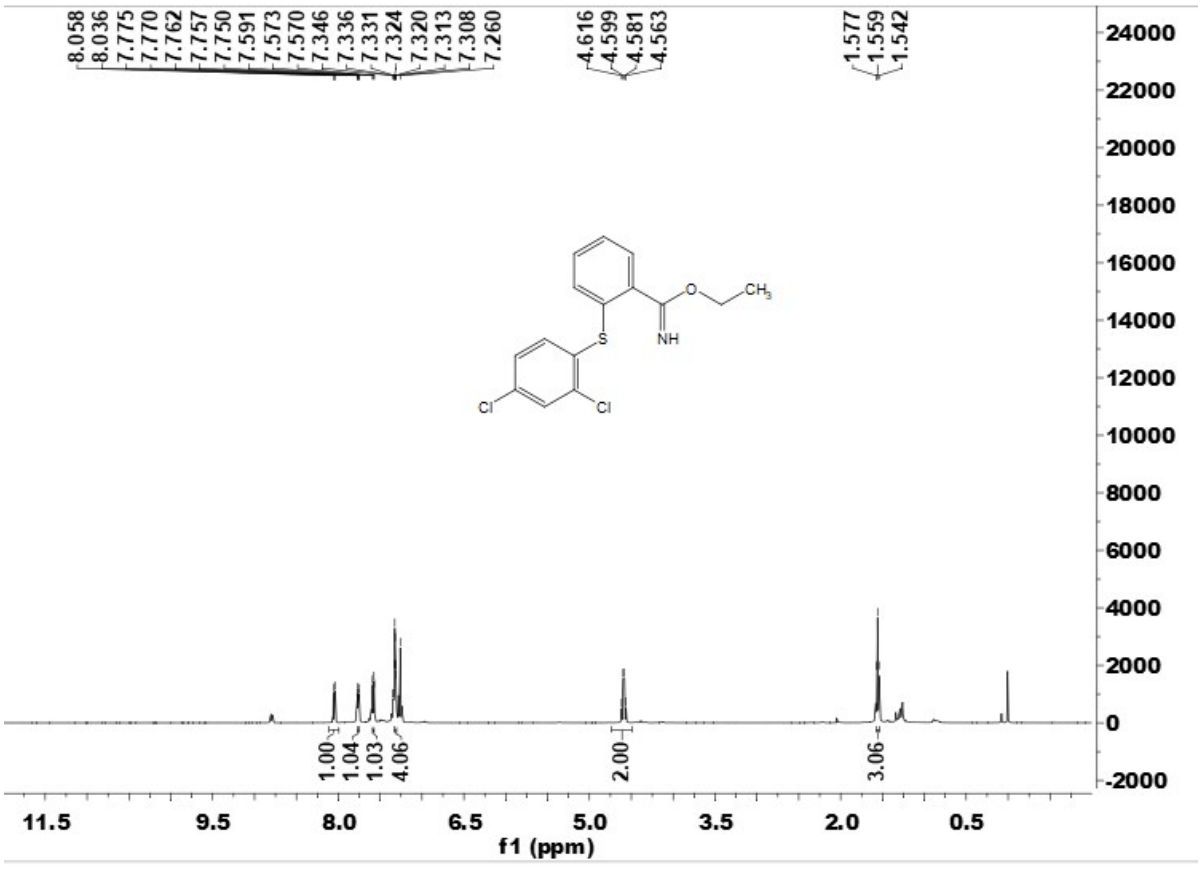


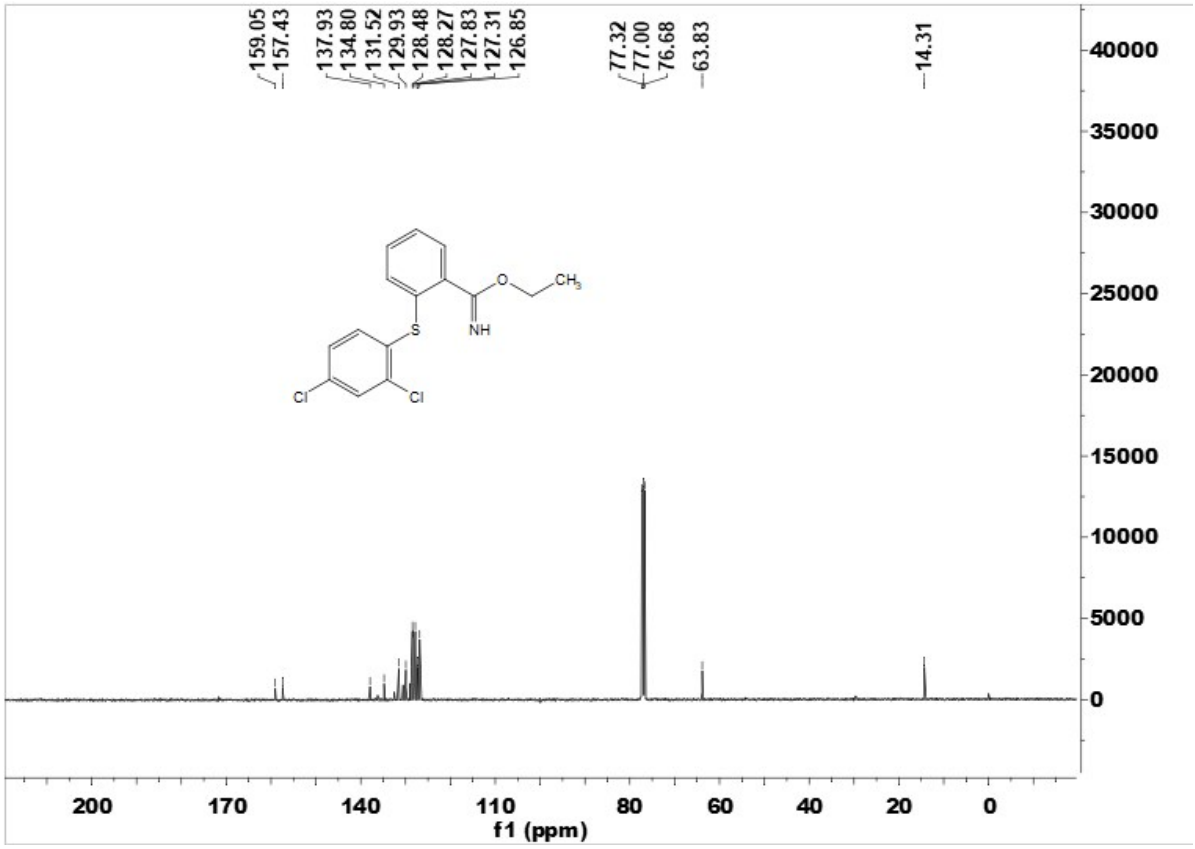
Ethyl 2-((4-bromophenyl)thio)benzimidate (4c),



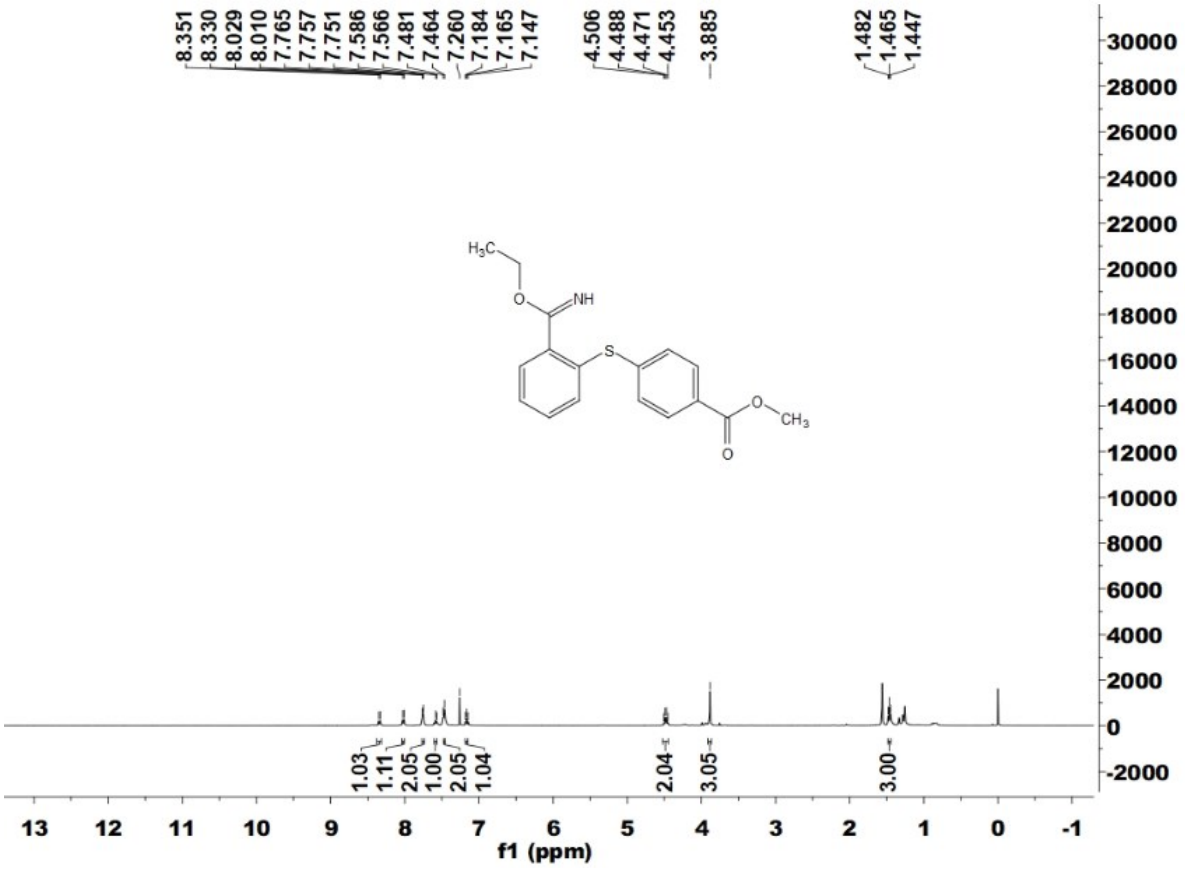


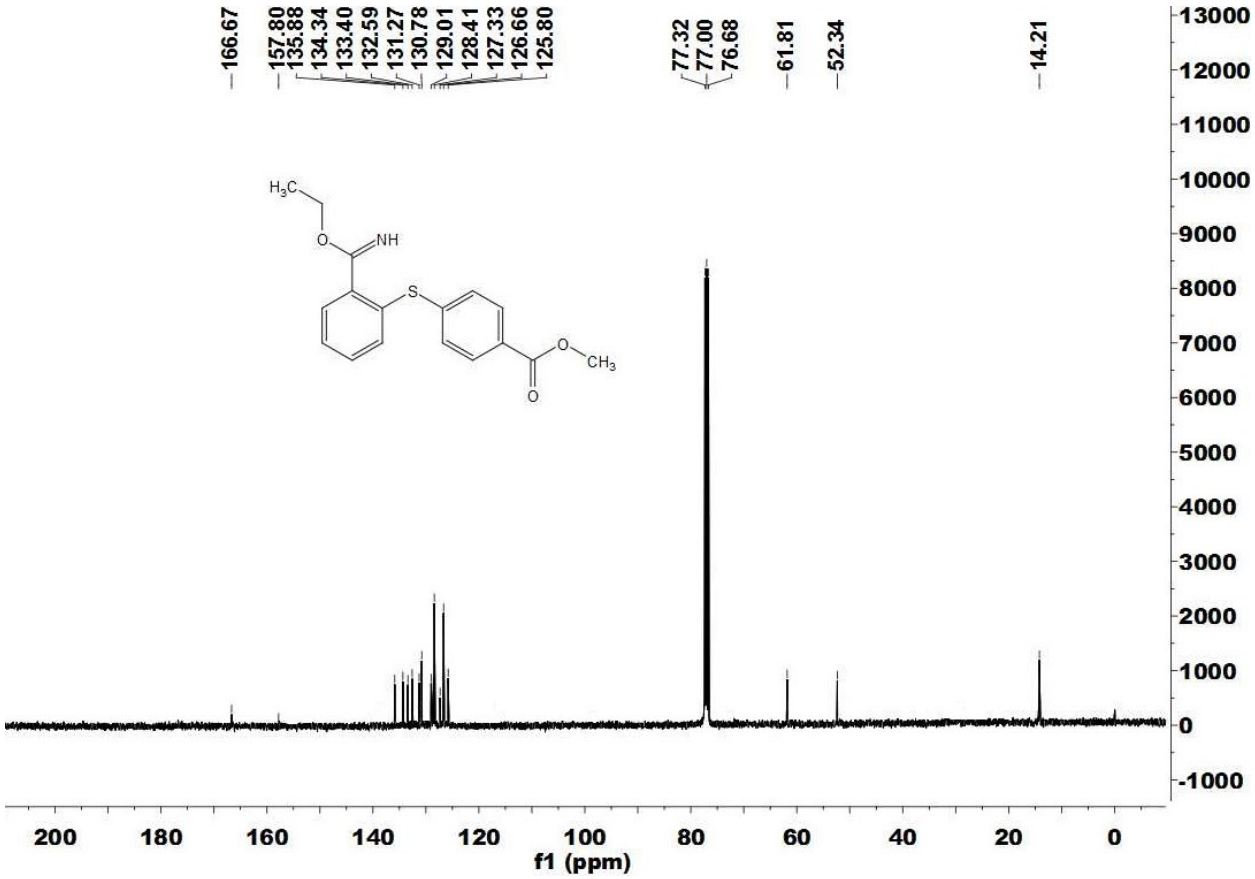
Ethyl 2-((2,4-dichlorophenyl)thio)benzimidate (4d)



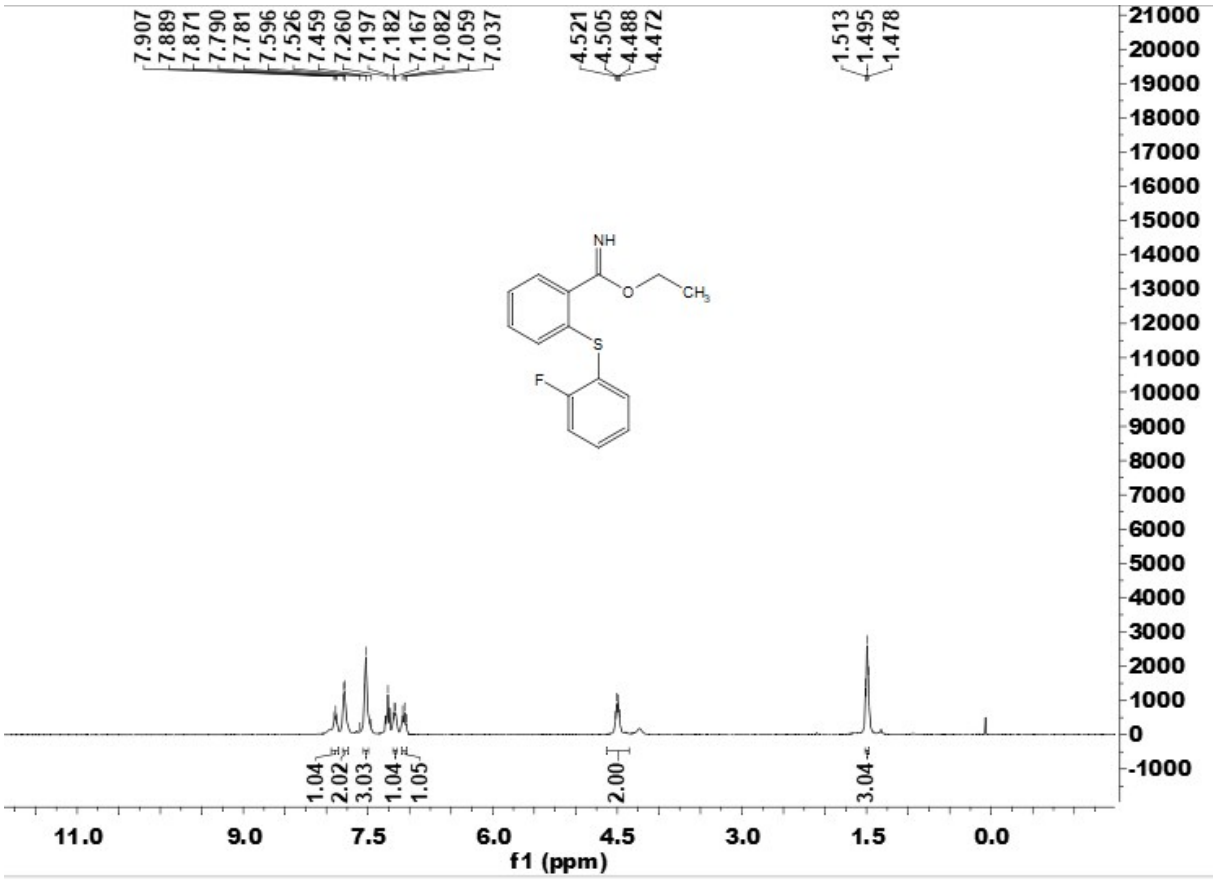


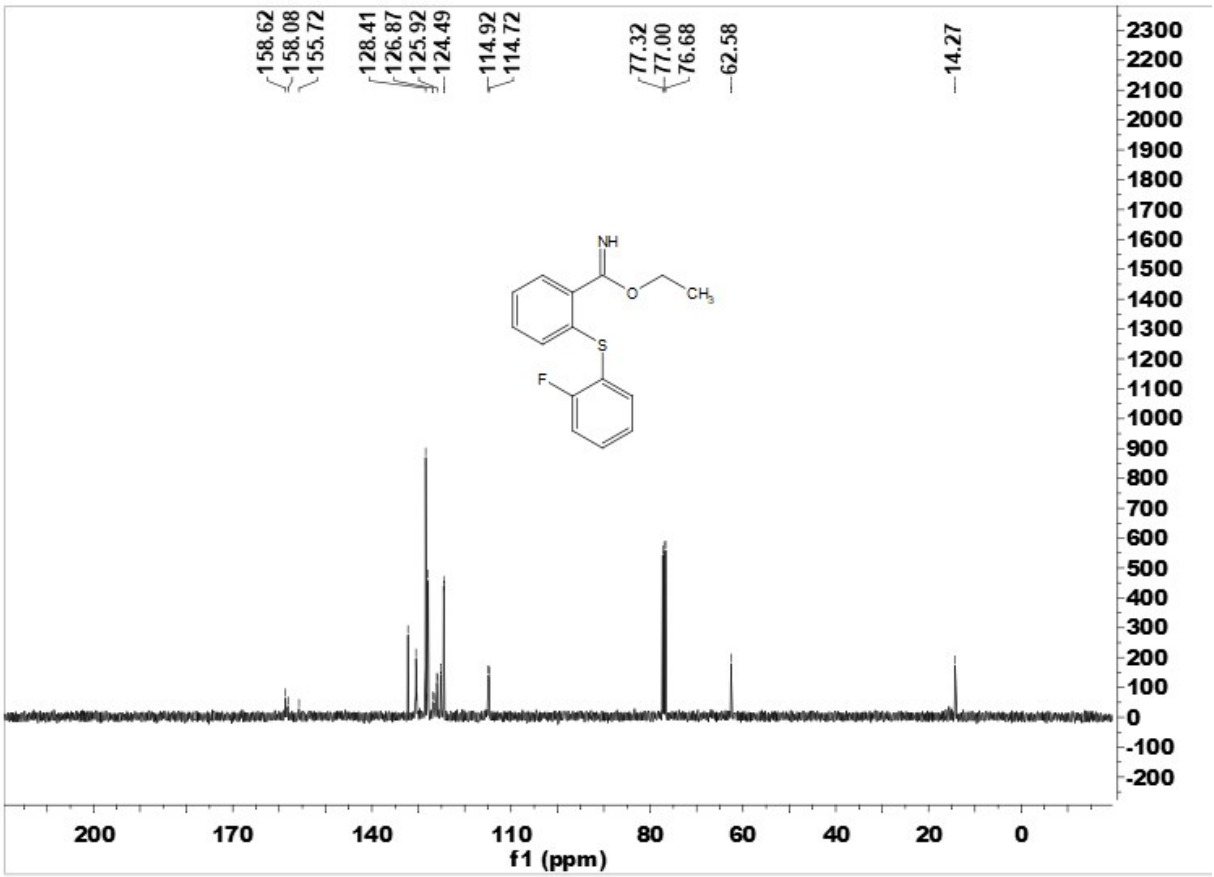
Methyl 4-((2-(ethoxy(imino)methyl)phenyl)thio)benzoate (4e)



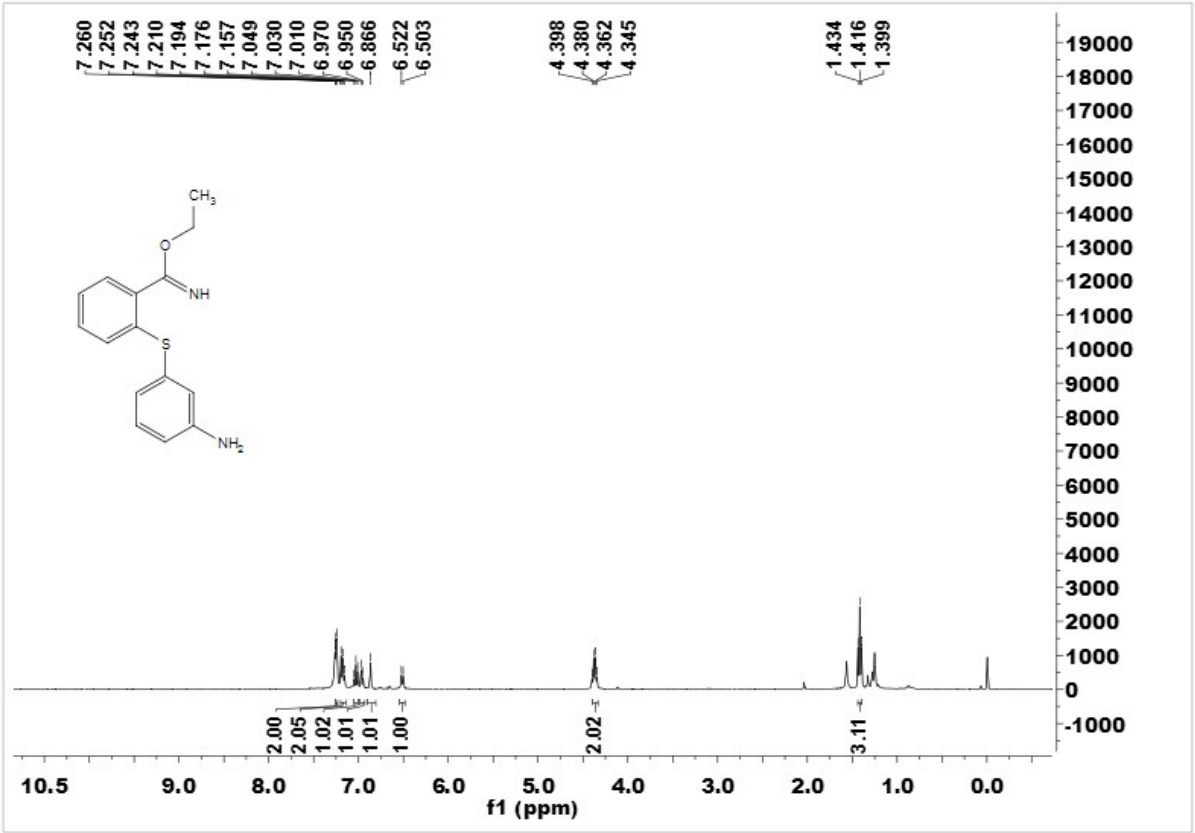


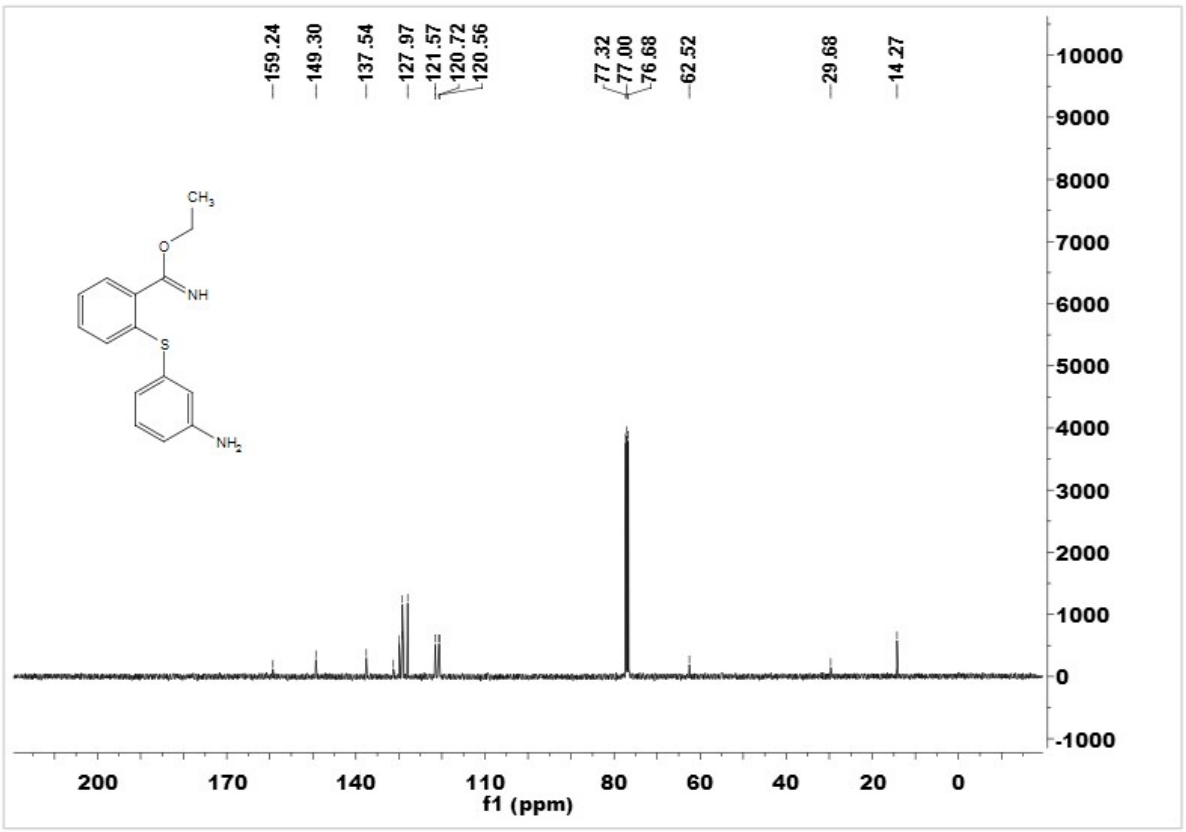
Ethyl 2-((2-fluorophenyl)thio)benzimidate (4f)



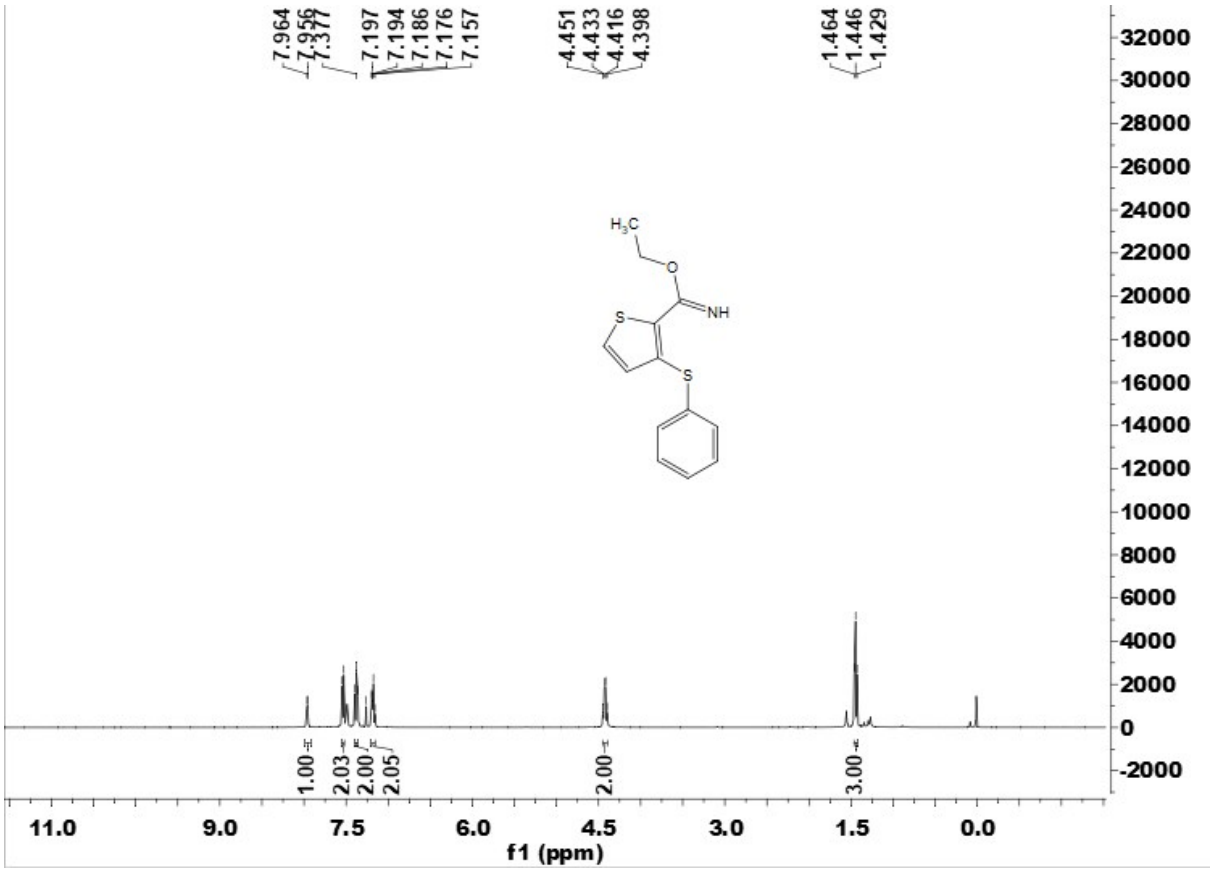


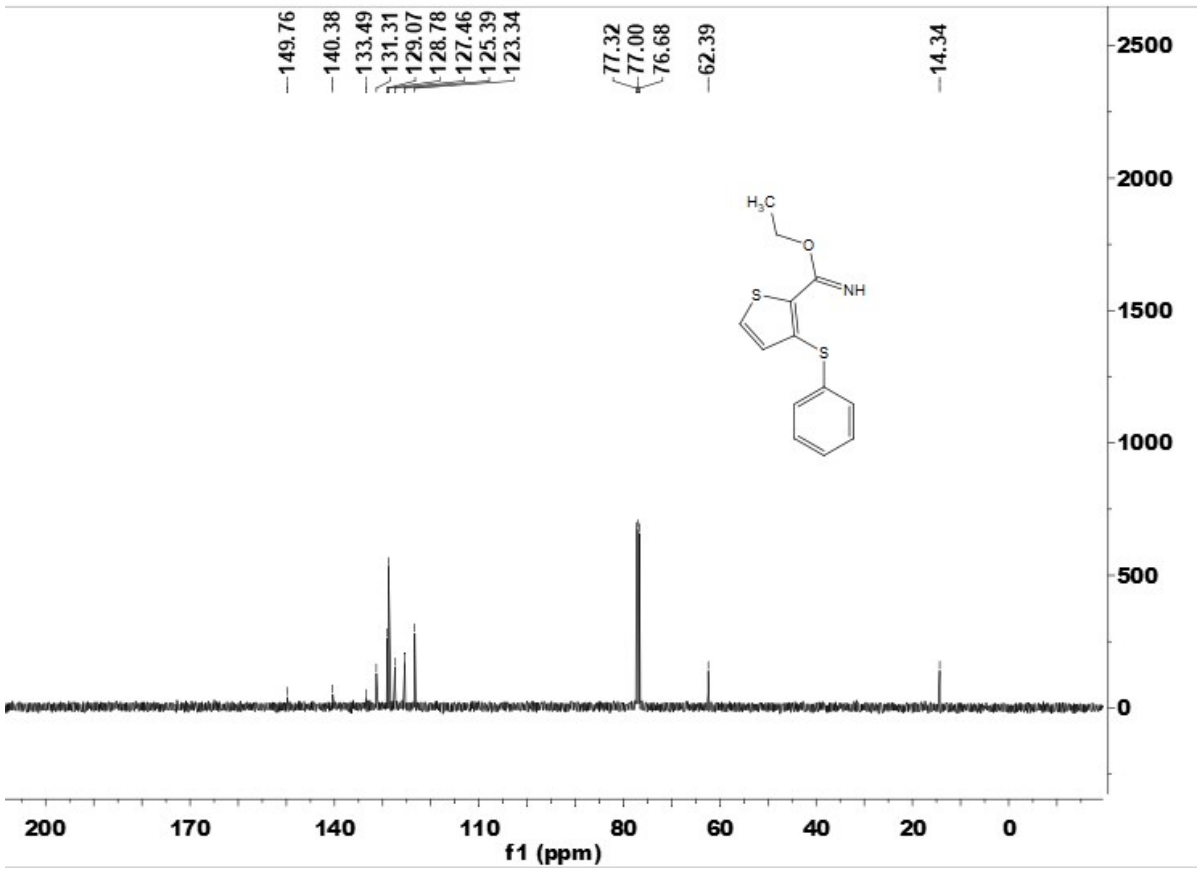
Ethyl 2-((3-aminophenyl)thio)benzimidate (4g)



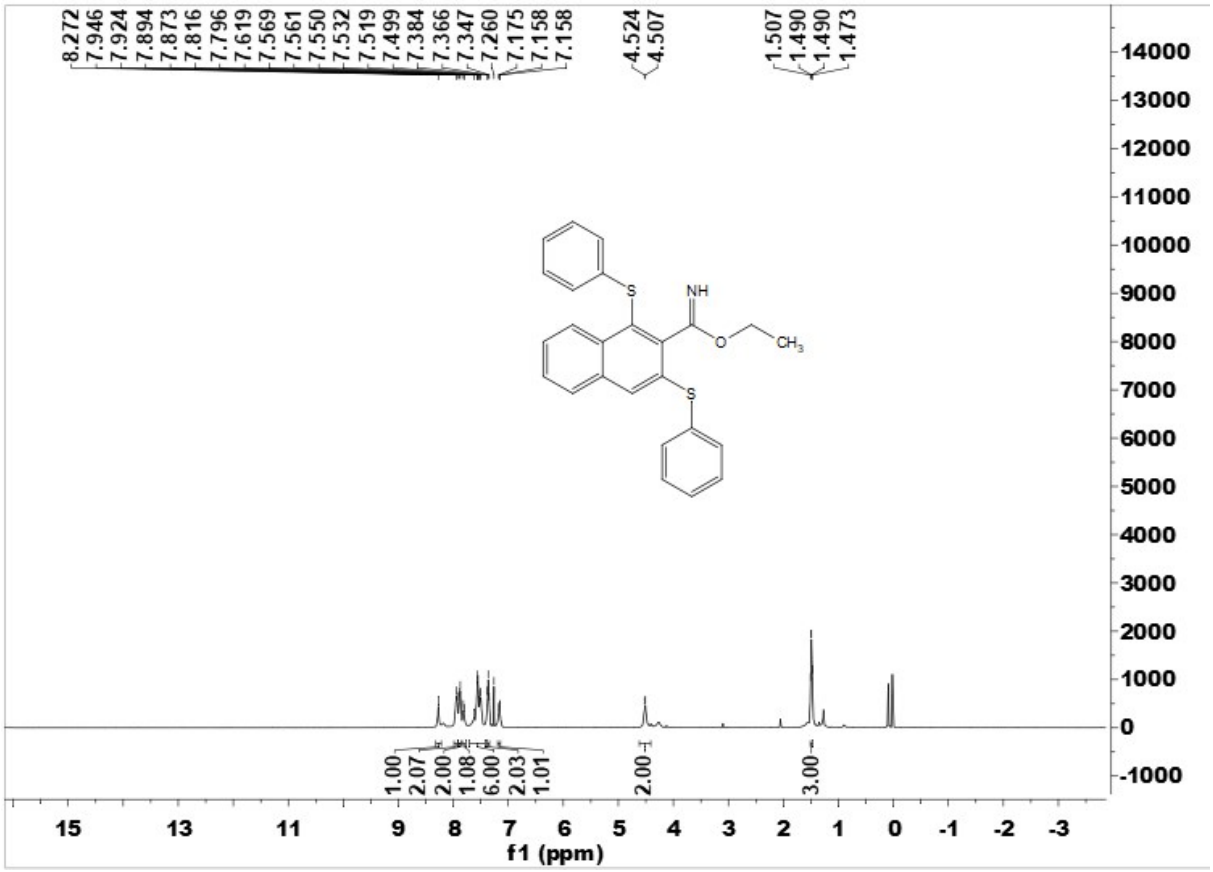


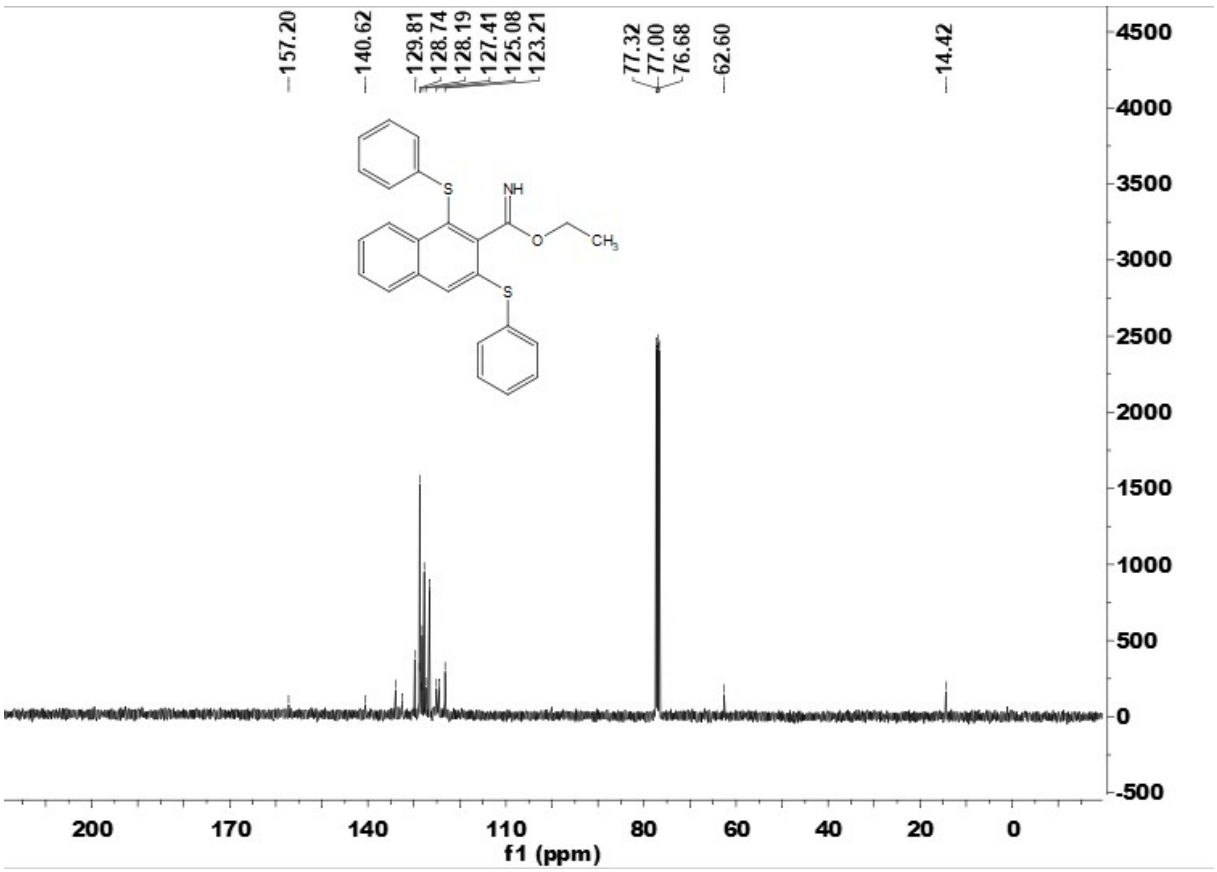
Ethyl 3-(phenylthio)thiophene-2-carbimidate (4h)



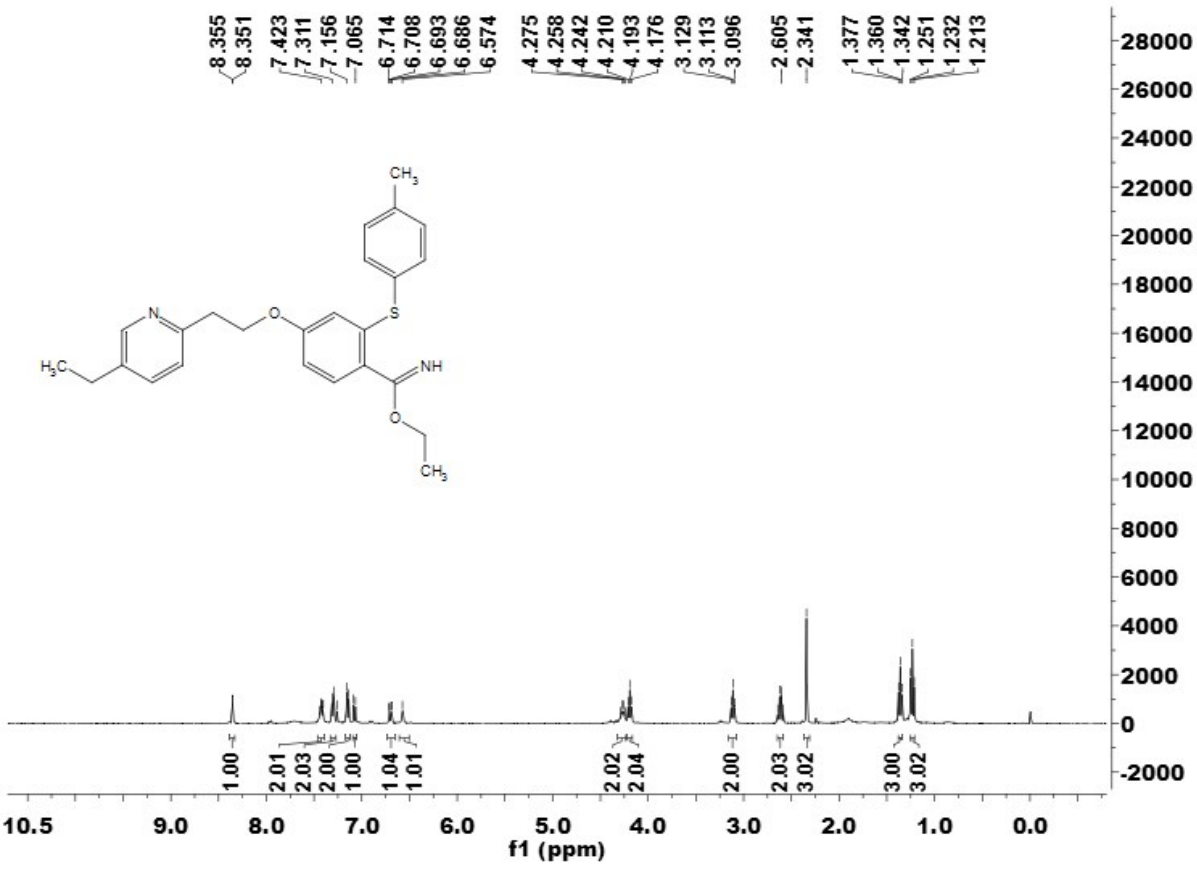


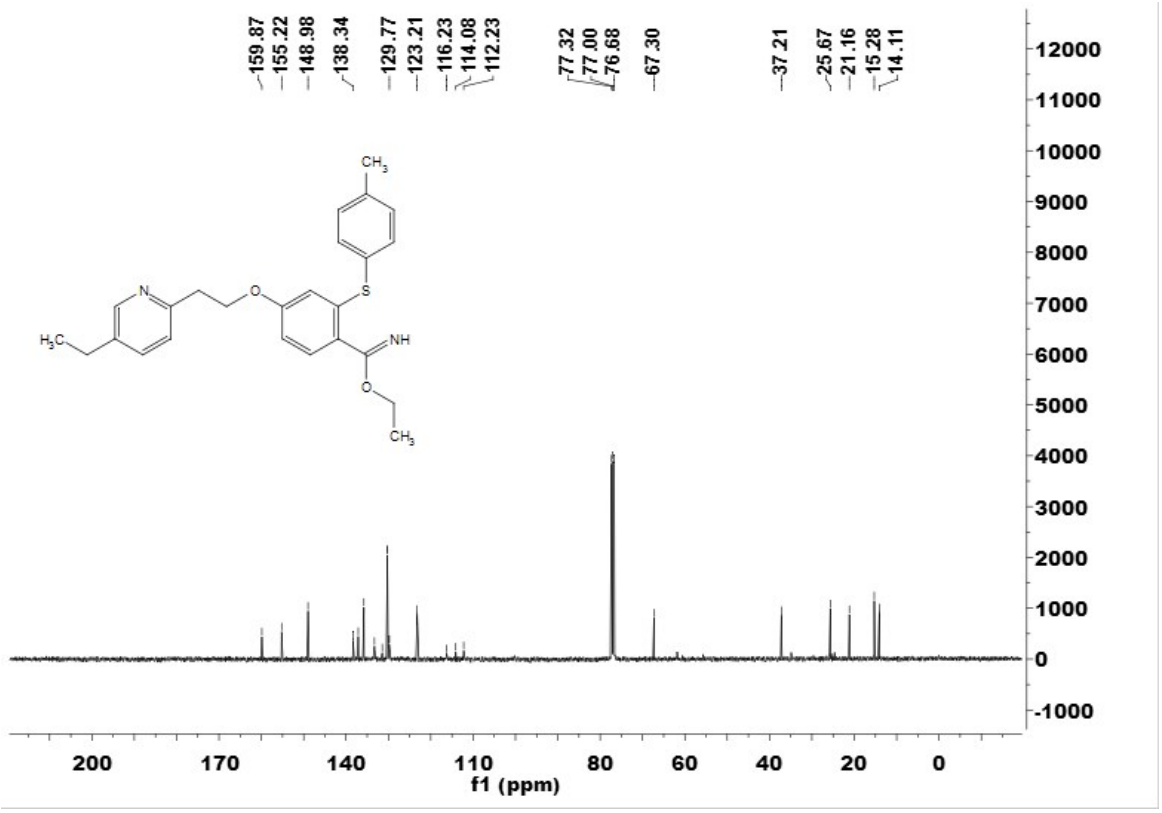
Ethyl 1,3-bis(phenylthio)-2-naphthimidate (4i)



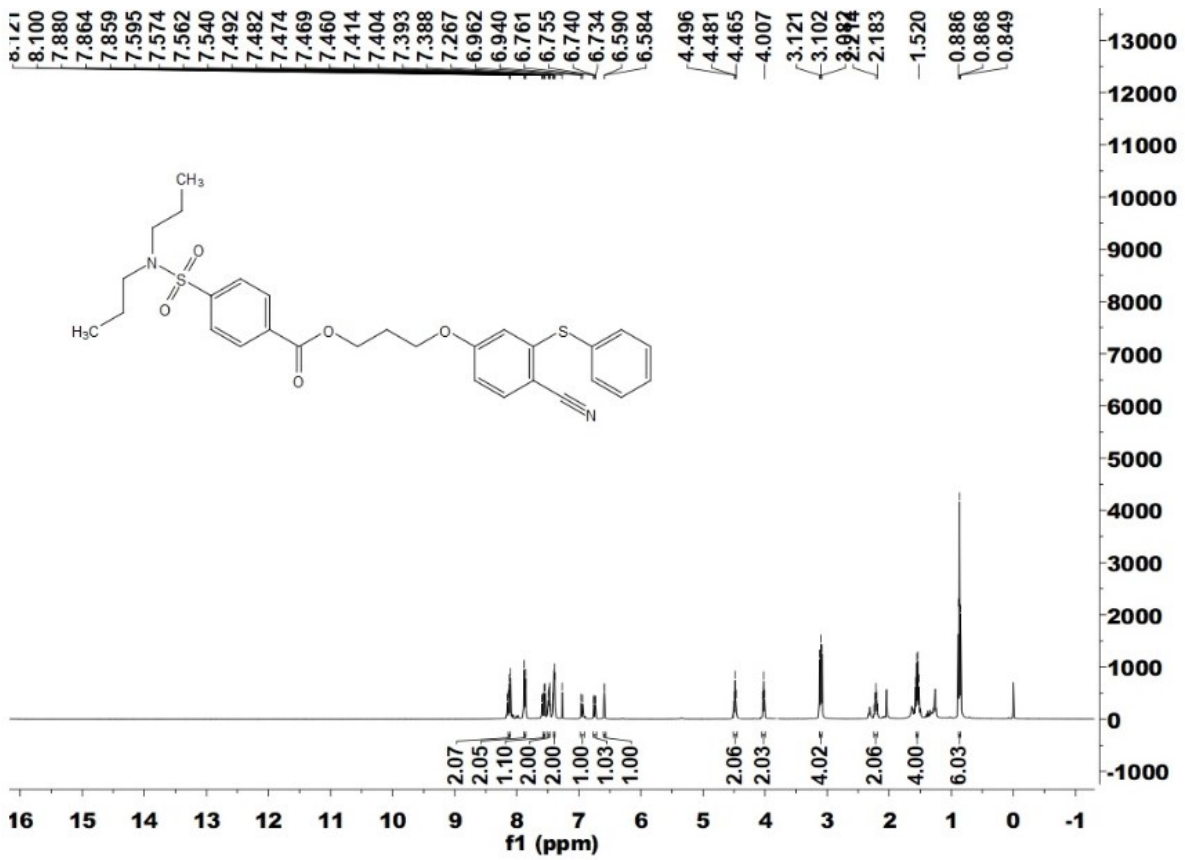


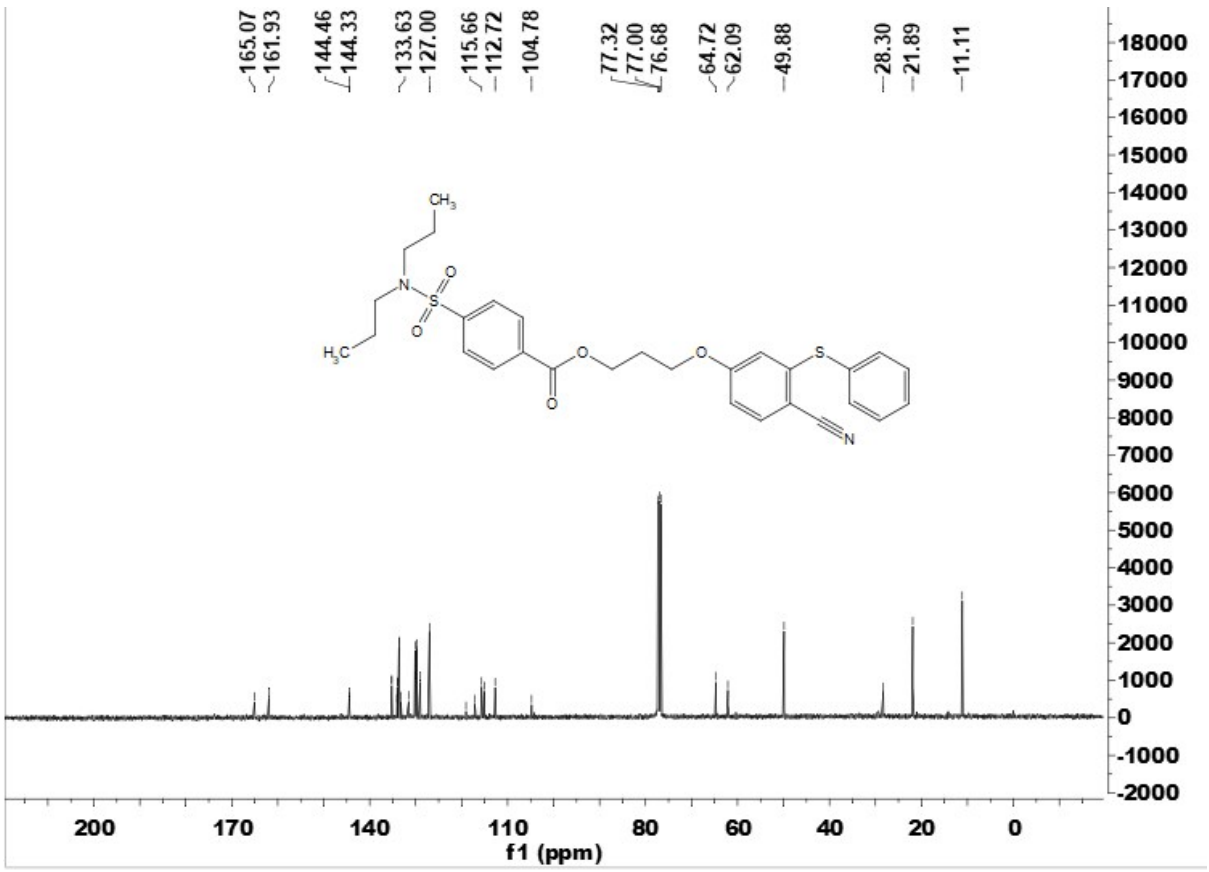
Ethyl 4-(2-(5-ethylpyridin-2-yl)ethoxy)-2-(*p*-tolylthio)benzimidate (4j)



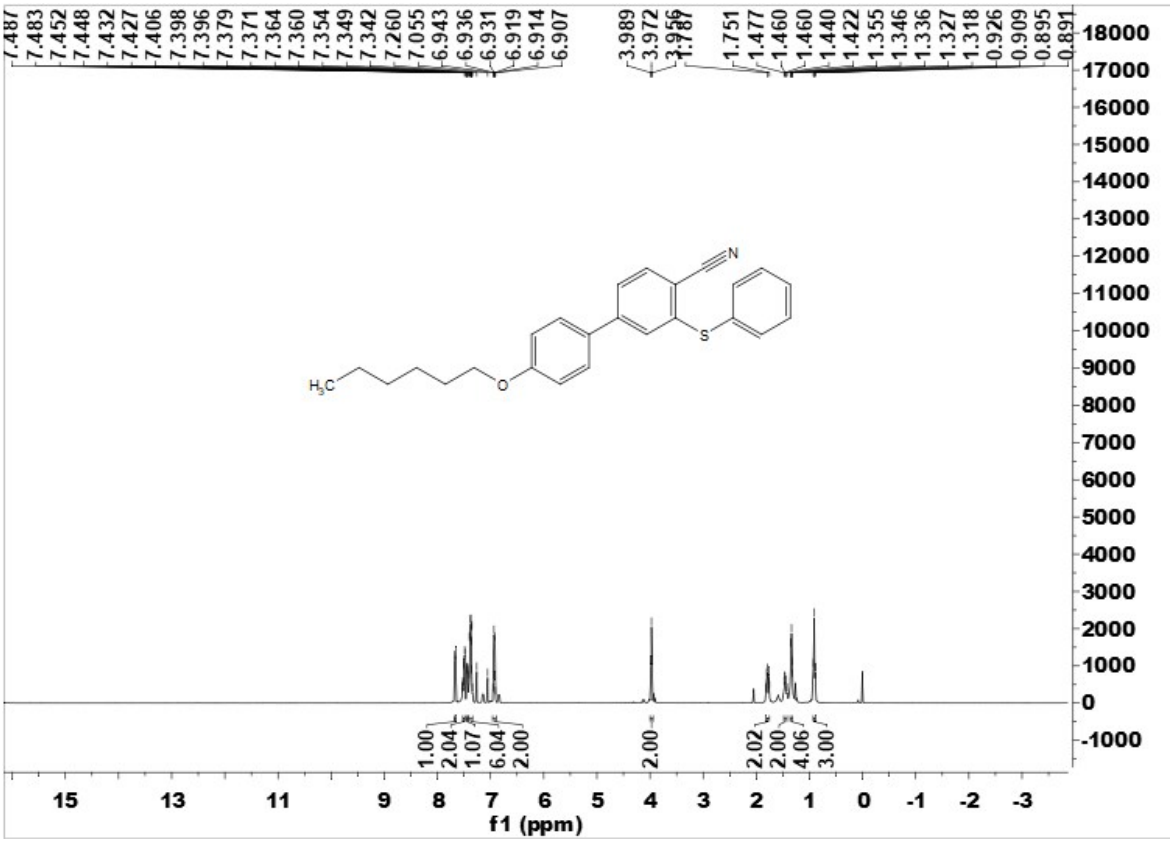


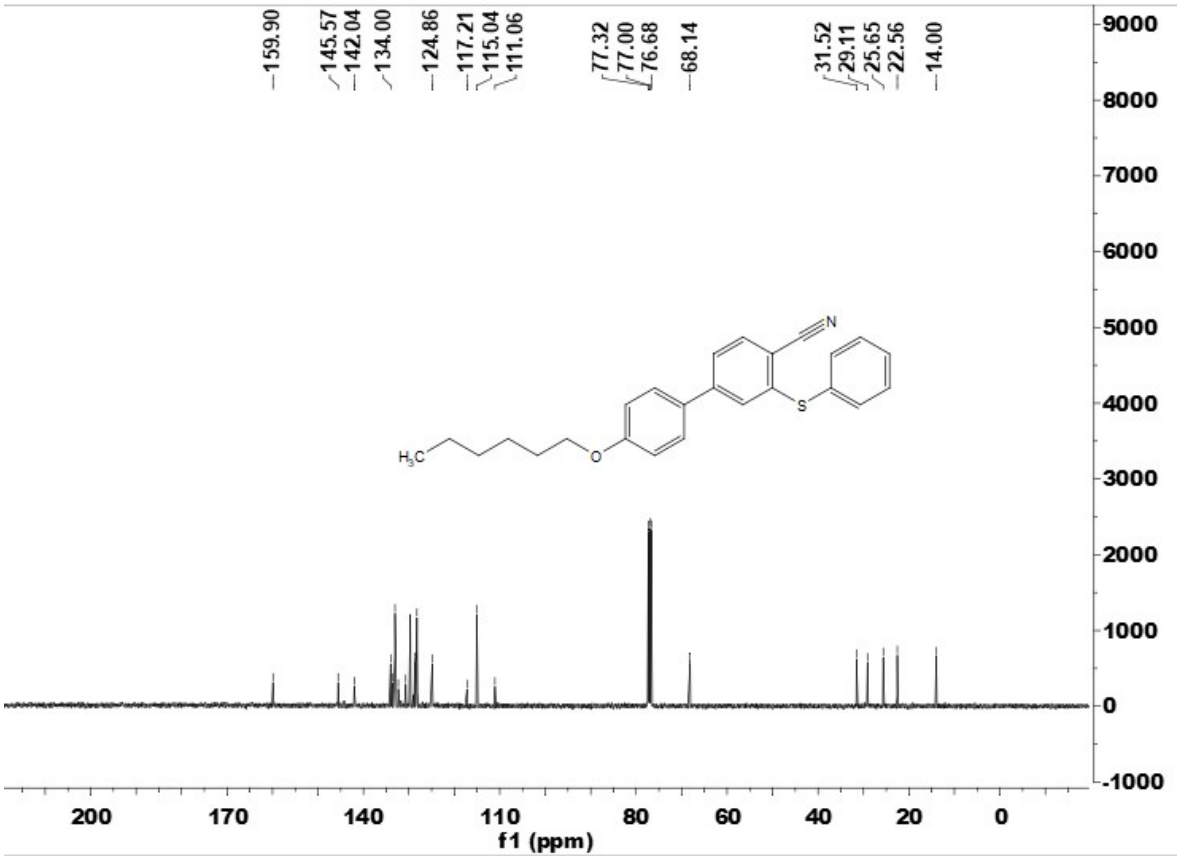
3-(4-Cyano-3-(phenylthio)phenoxy)propyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (3zb)



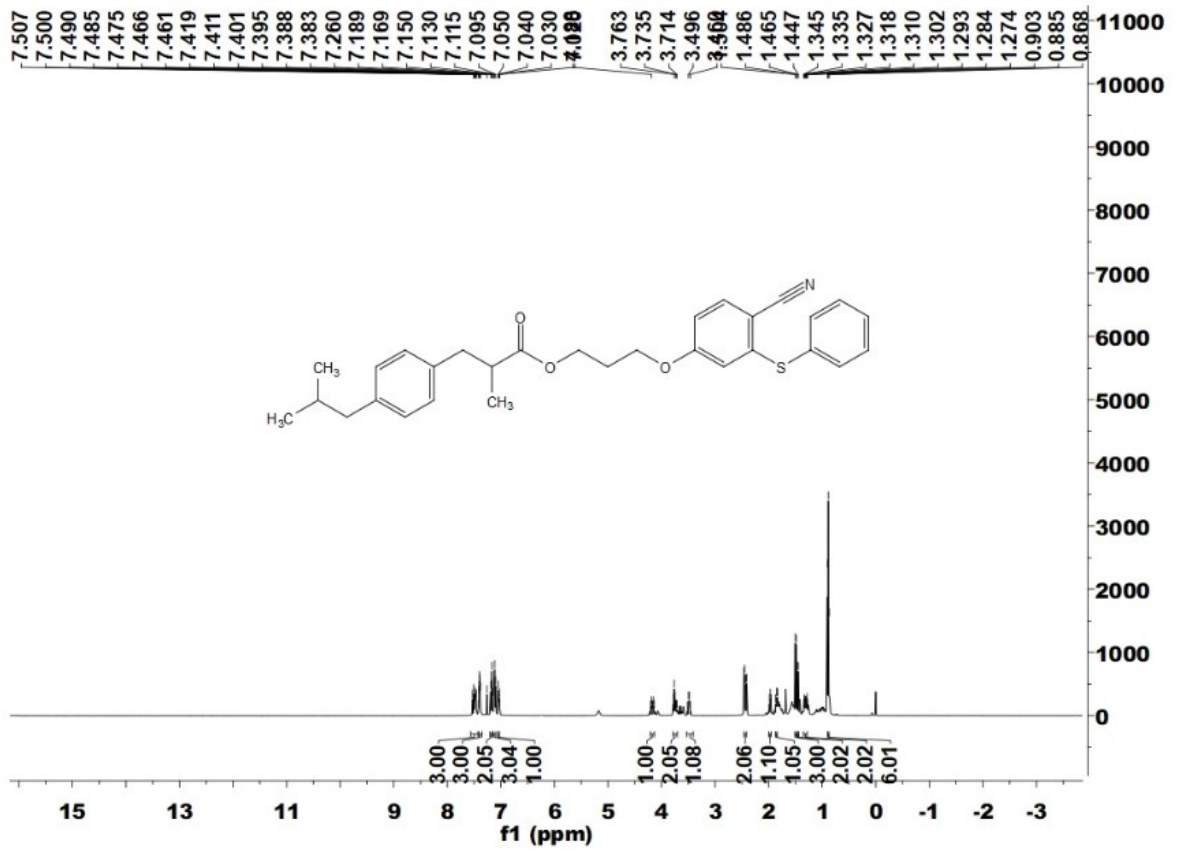


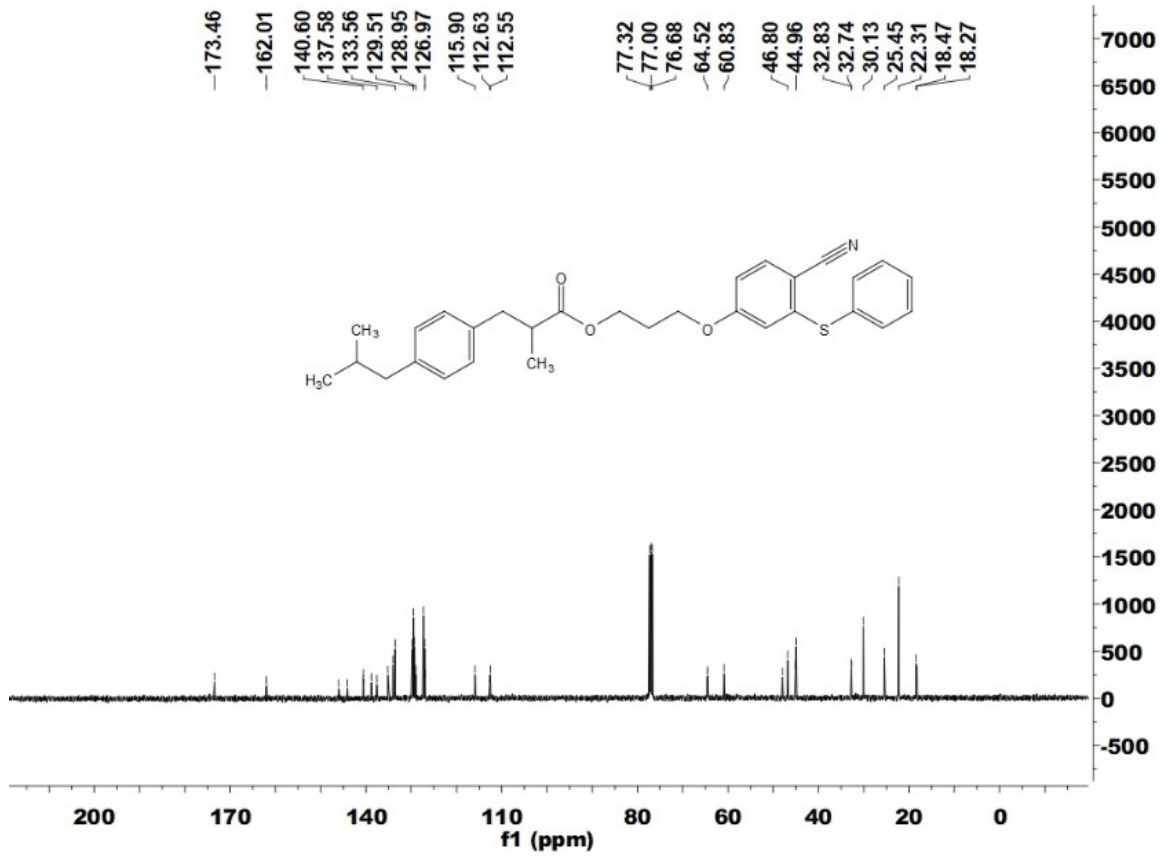
4'-(Hexyloxy)-3-(phenylthio)-[1,1'-biphenyl]-4-carbonitrile (3zc)



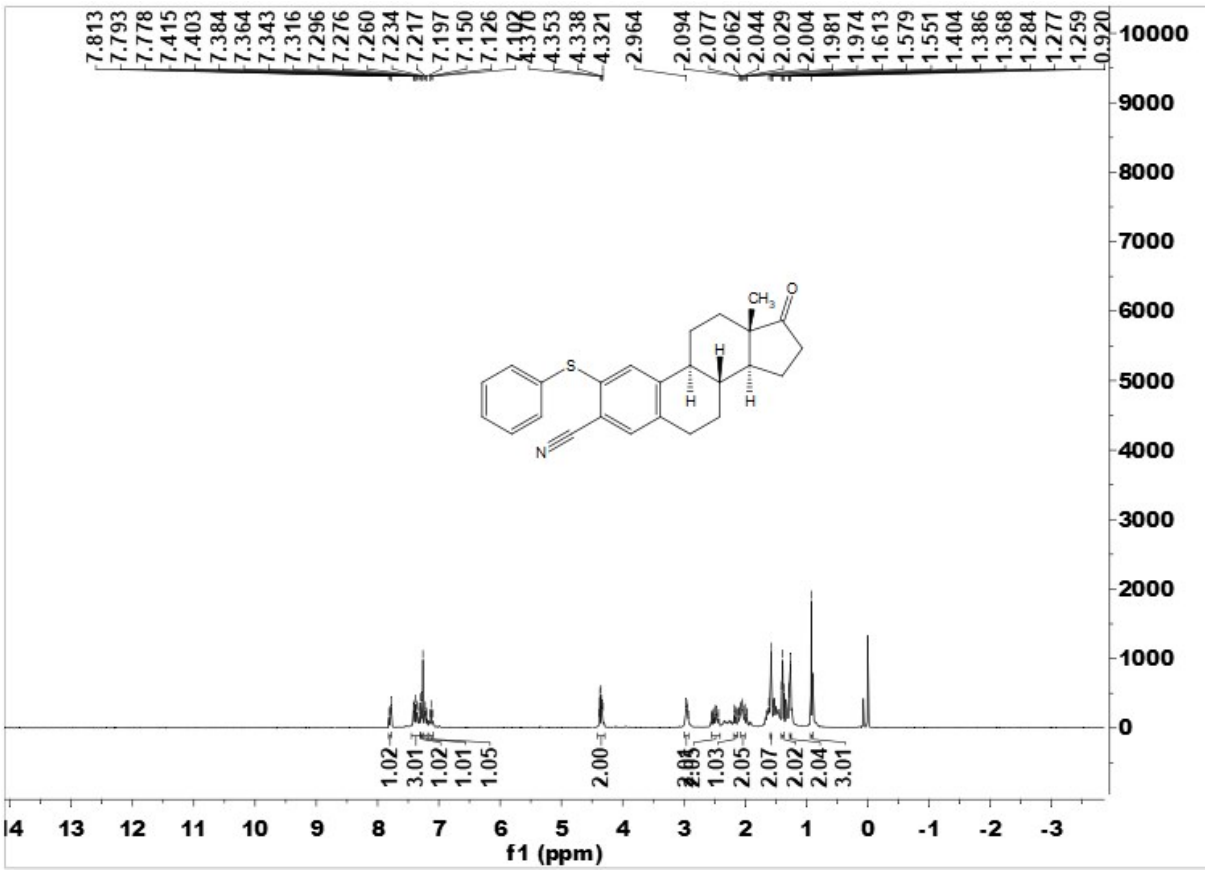


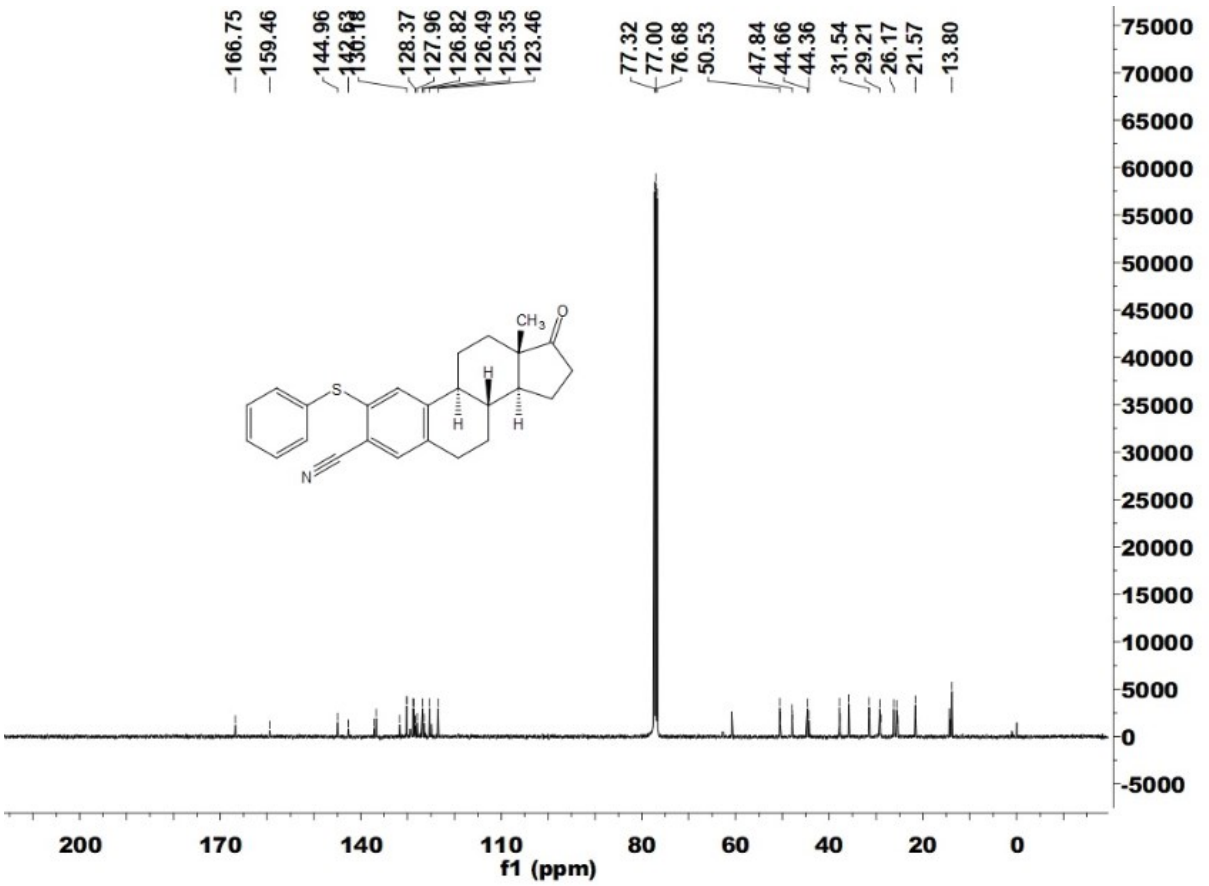
3-(4-Cyano-3-(phenylthio)phenoxy)propyl 3-(4-isobutylphenyl)-2-methylpropanoate (3zd)



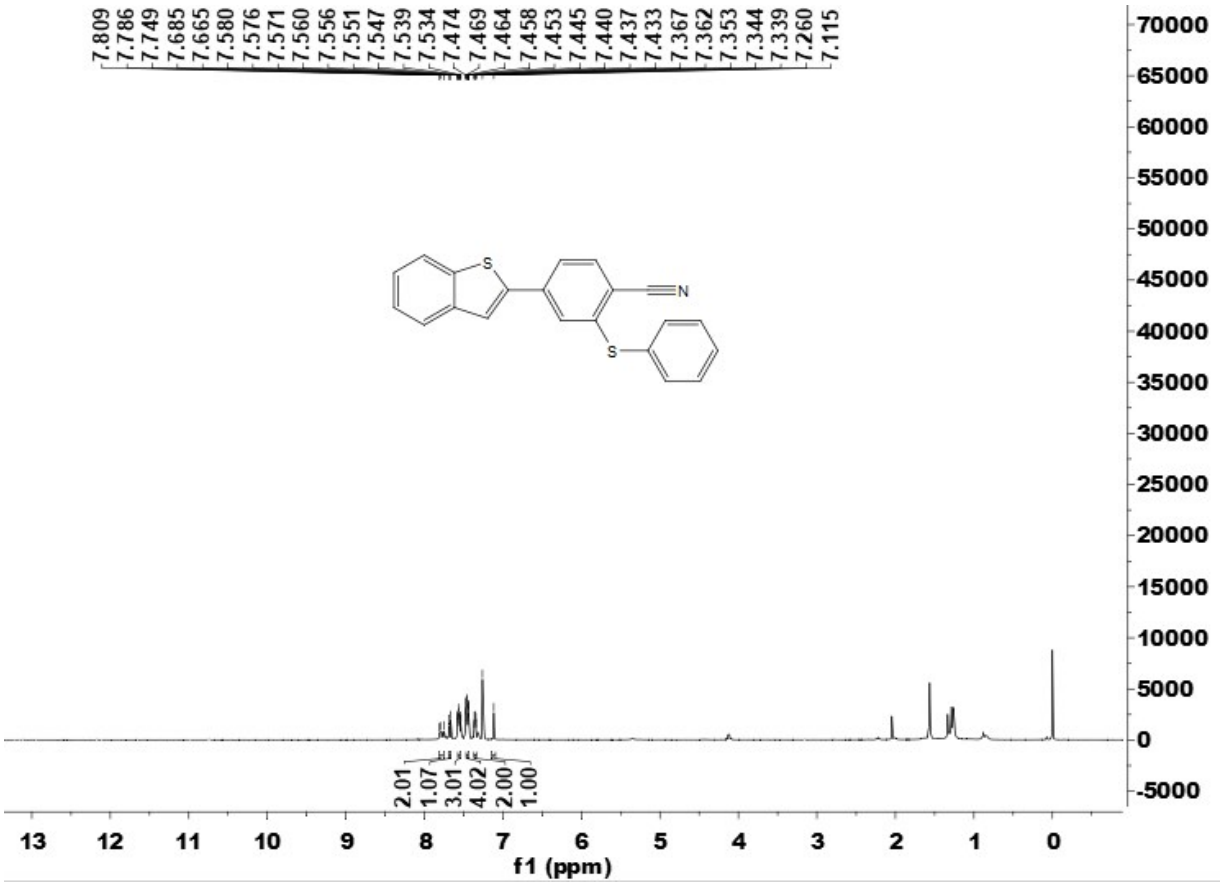


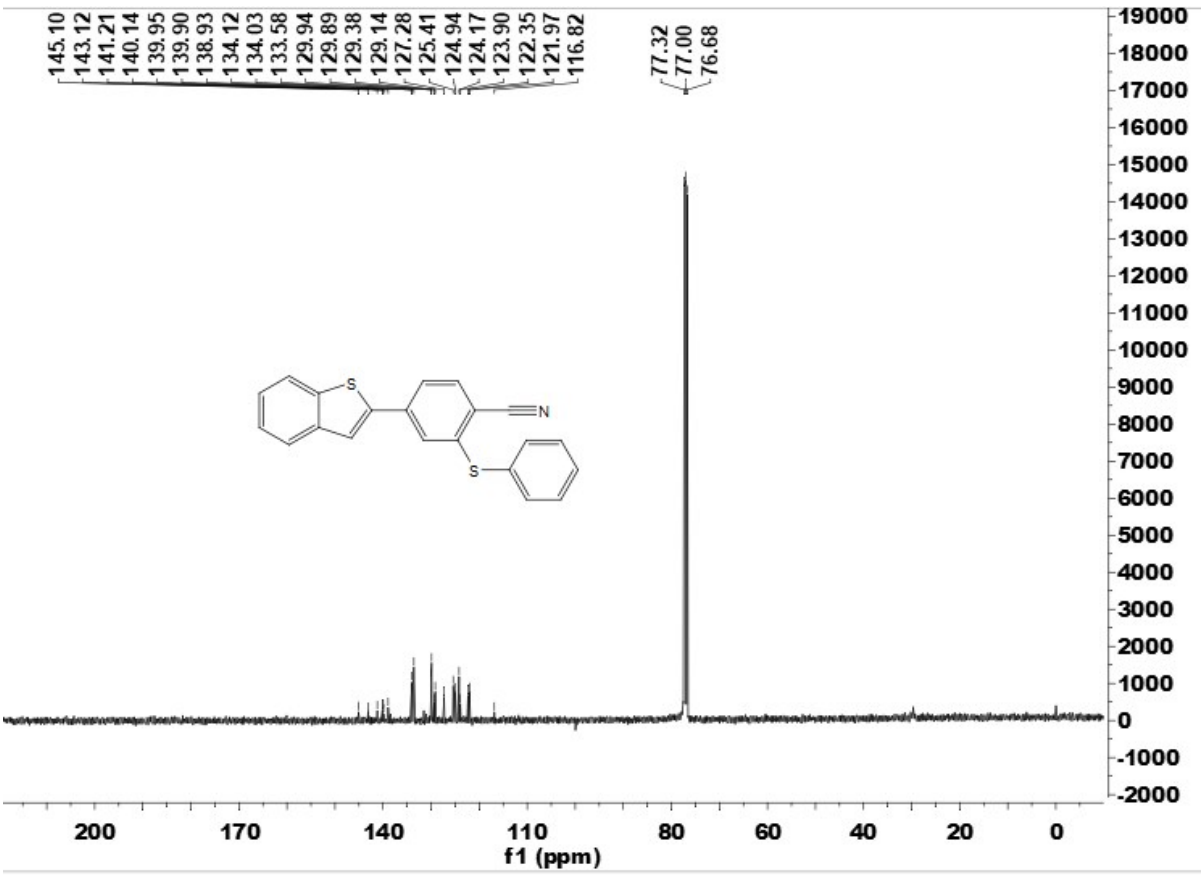
(8*R*,9*S*,13*S*,14*S*)-13-Methyl-17-*oxo*-2-(phenylthio)-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthrene-3-carbonitrile (3ze)



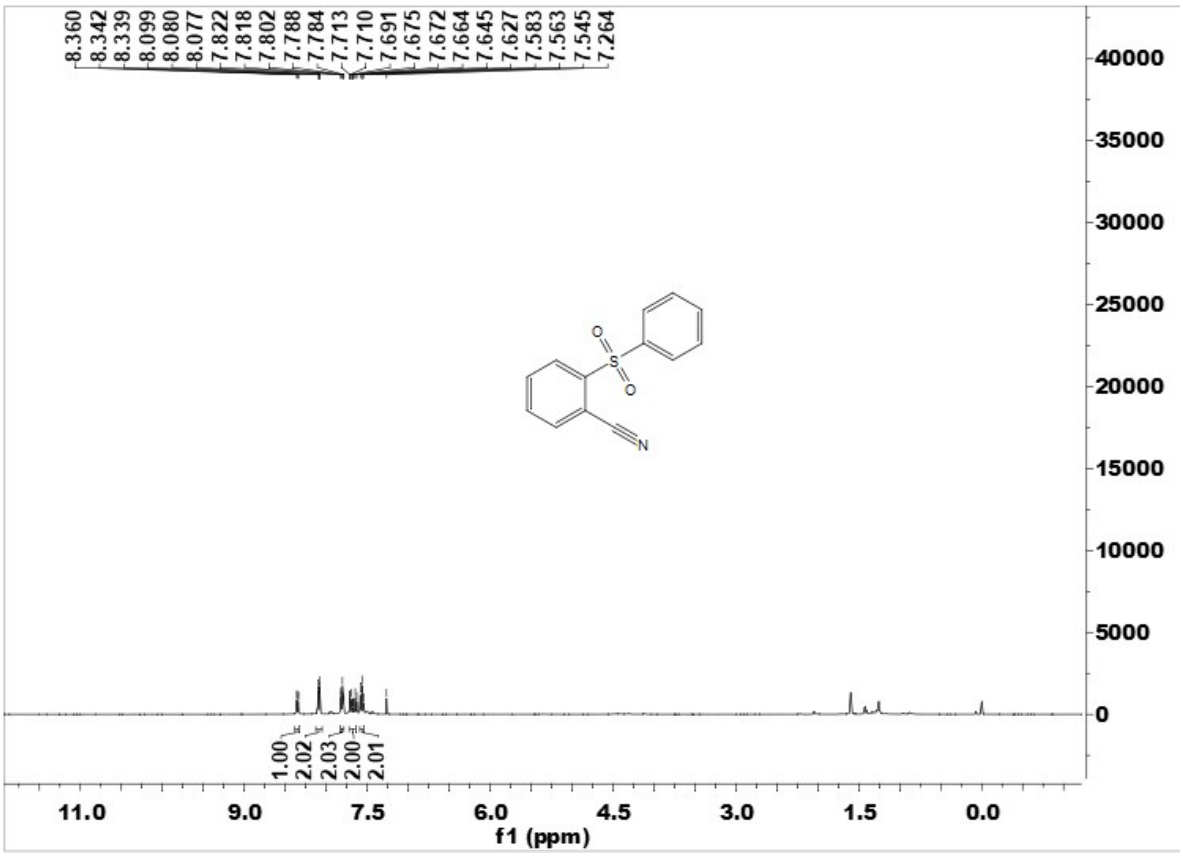


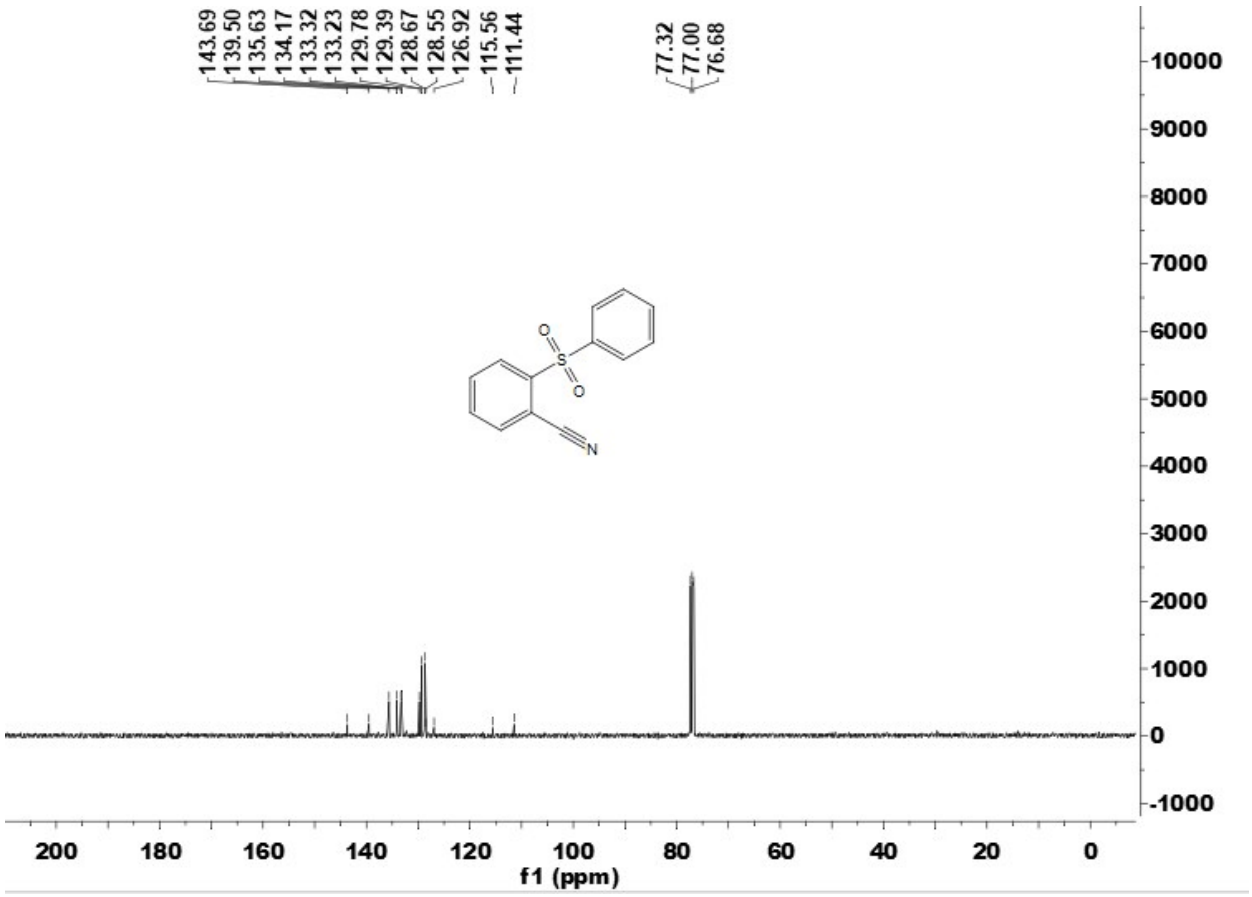
4-(Benzo[*b*]thiophen-2-yl)-2-(phenylthio)benzonitrile (5)



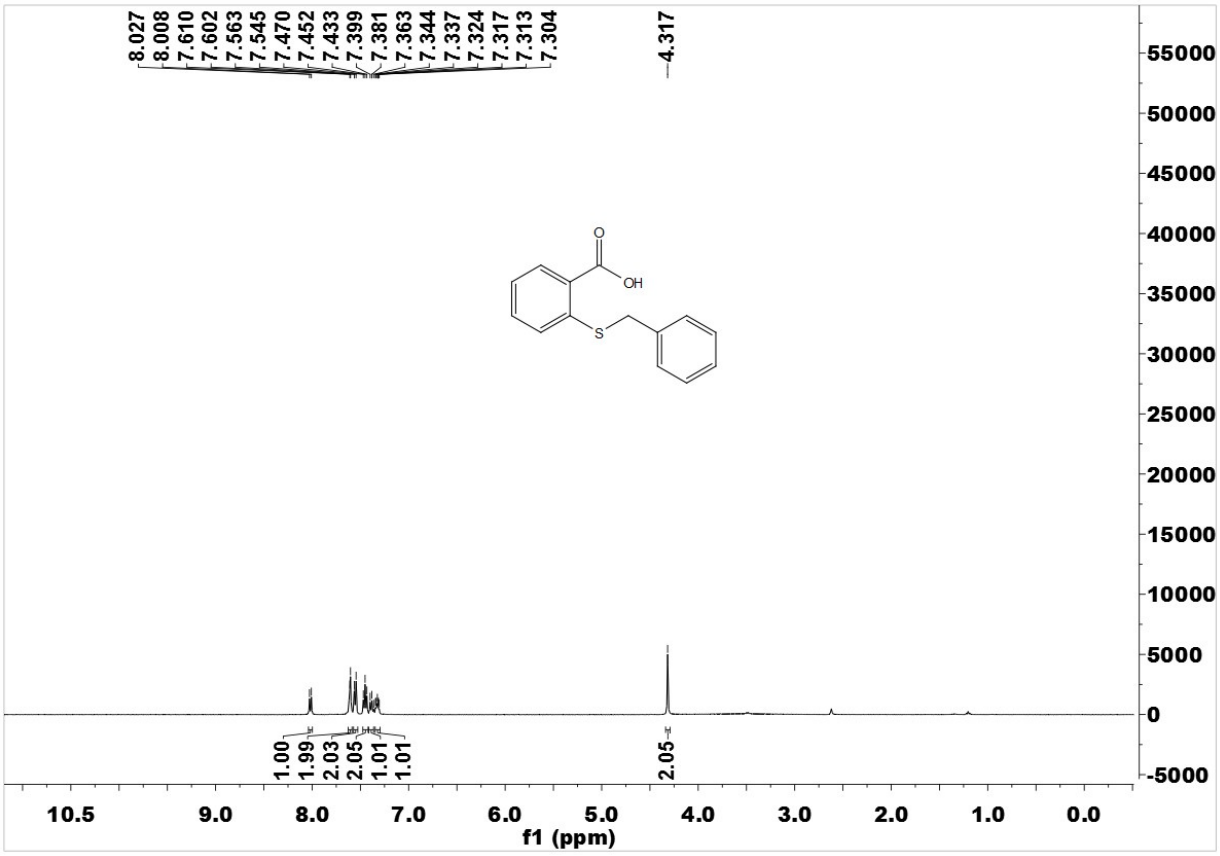


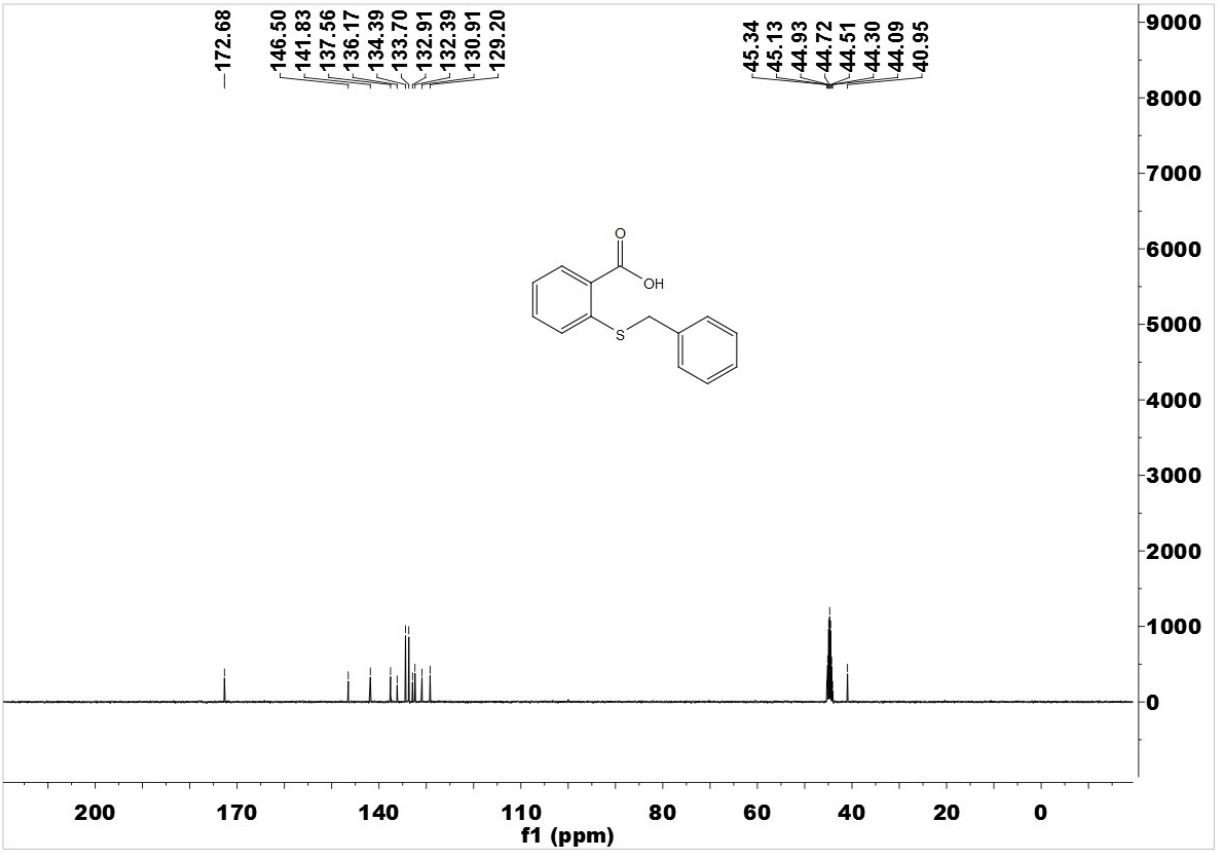
2-(Phenylsulfonyl)benzonitrile (6)



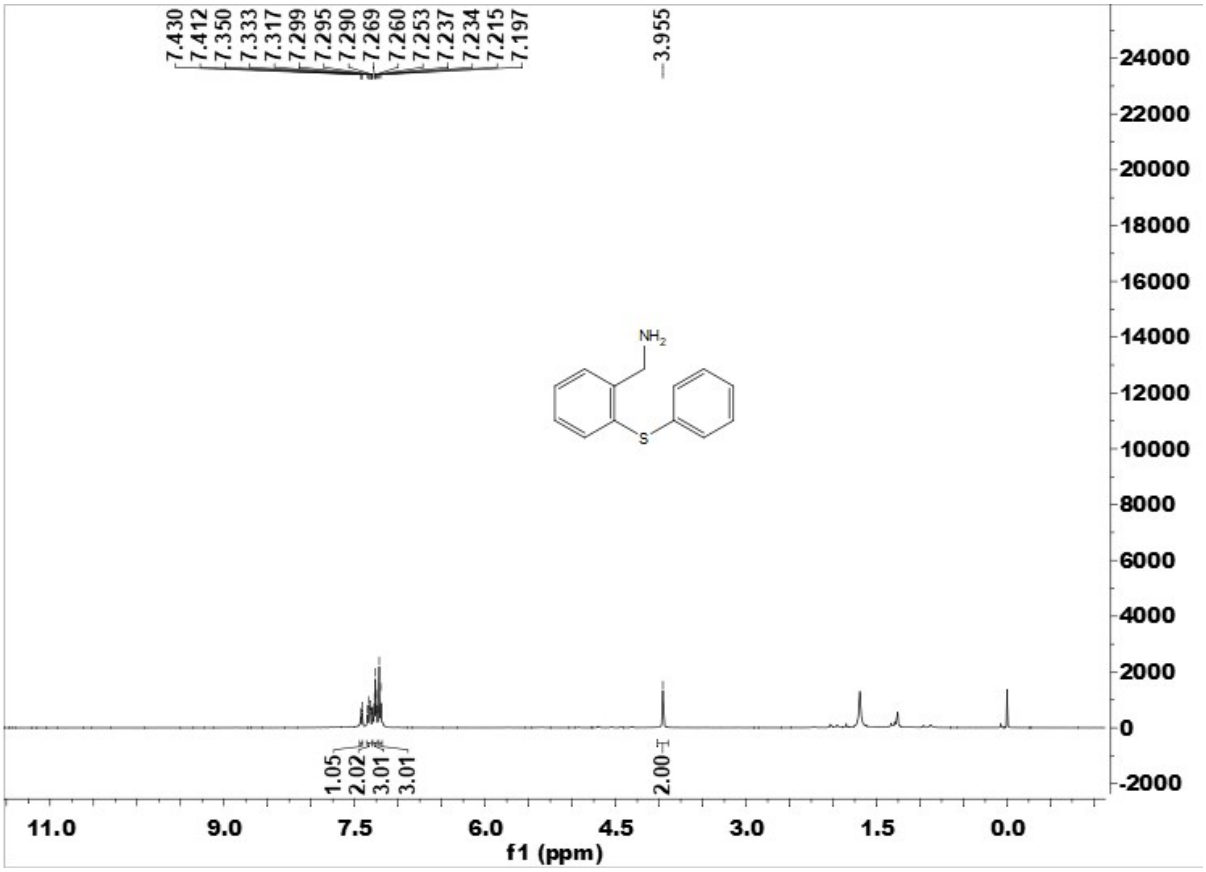


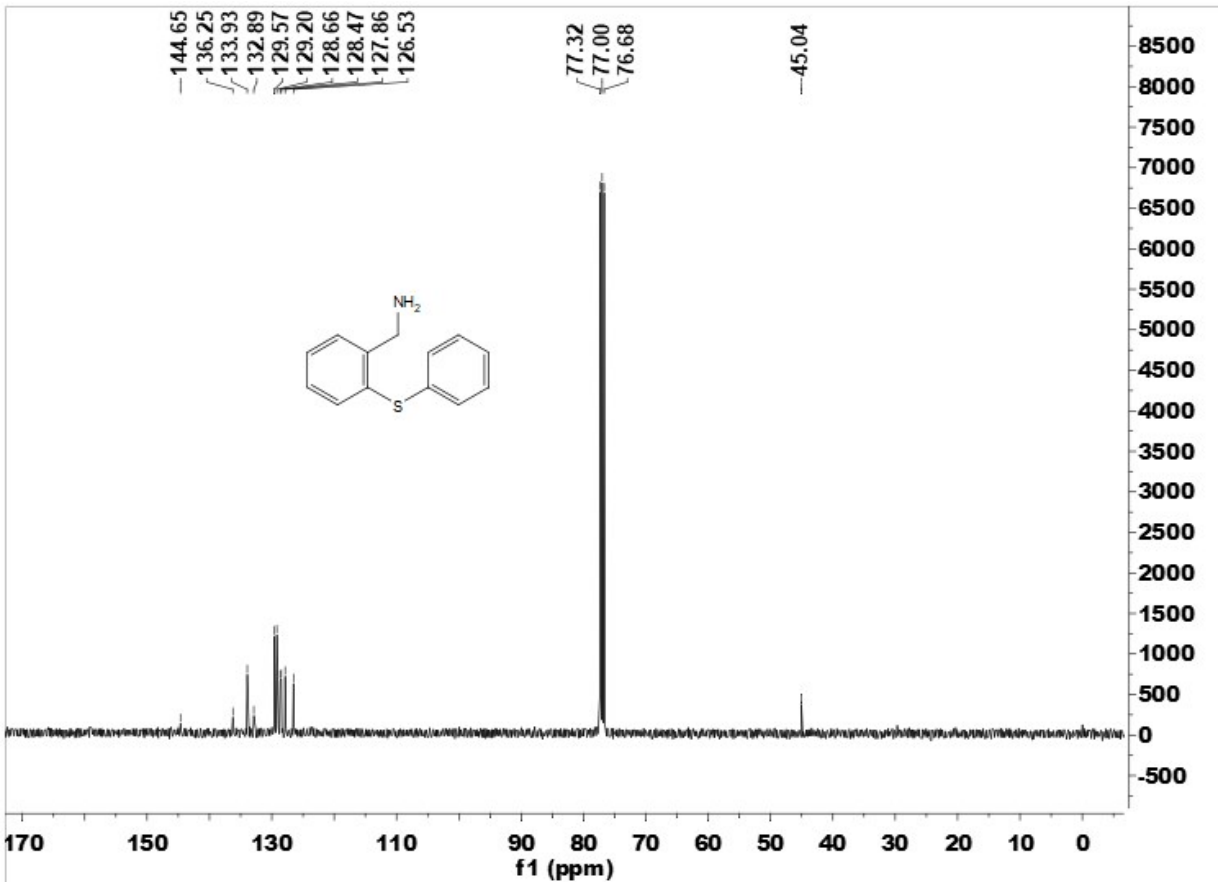
2-(Benzylthio)benzoic acid (7)



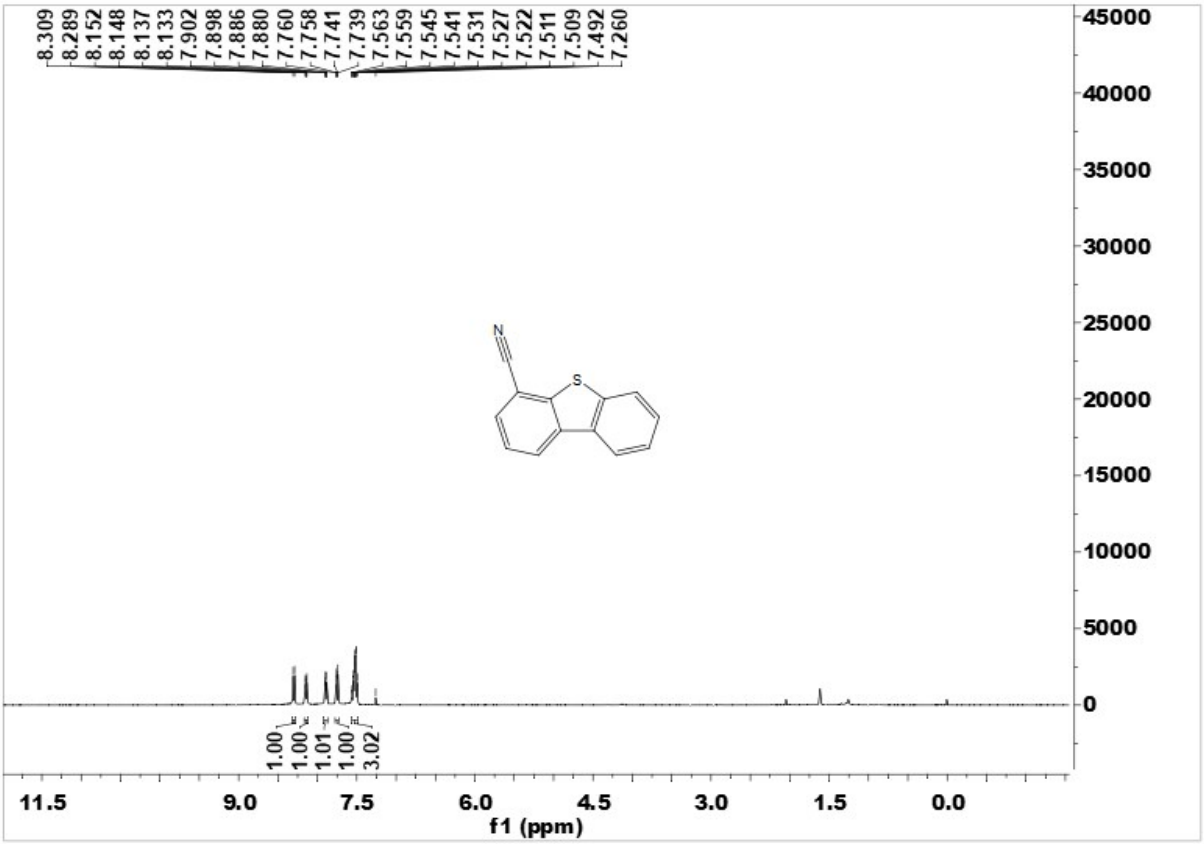


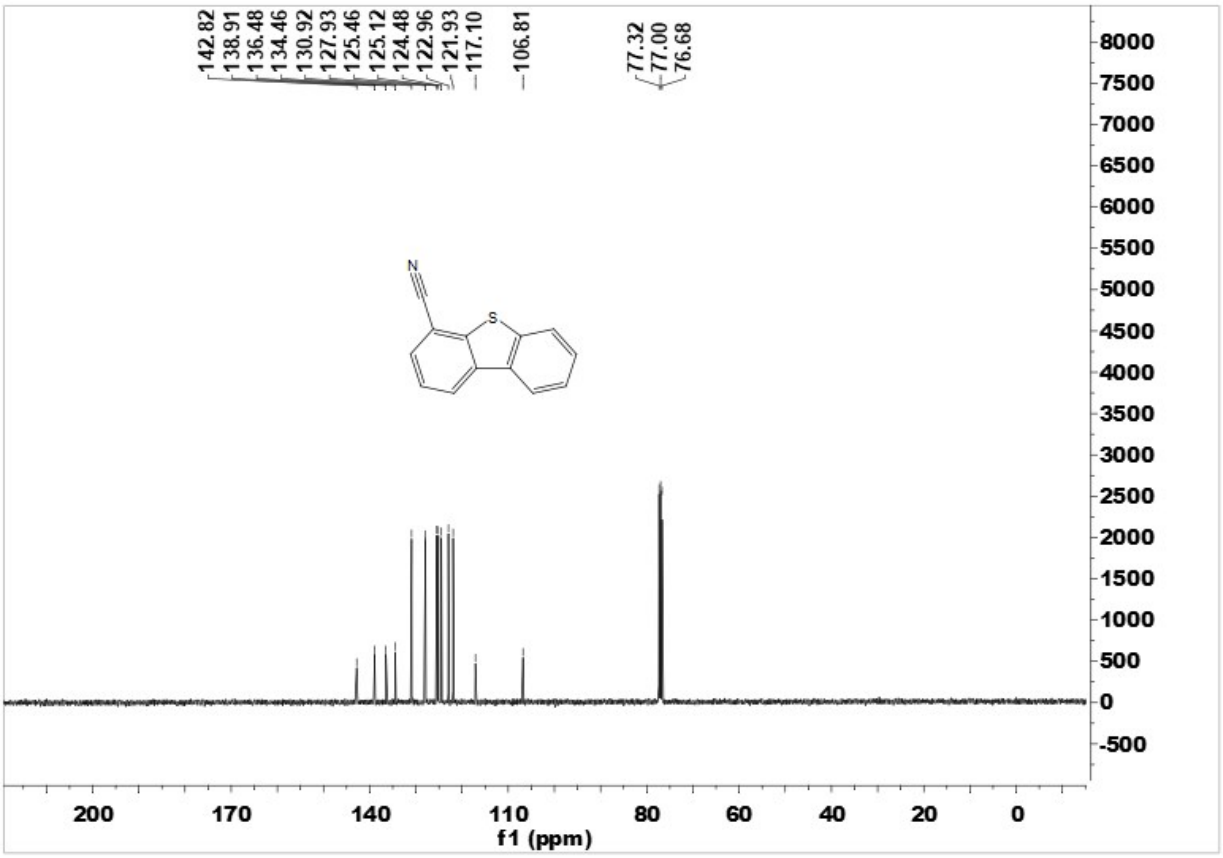
(2-(Phenylthio)phenyl)methanamine (8)



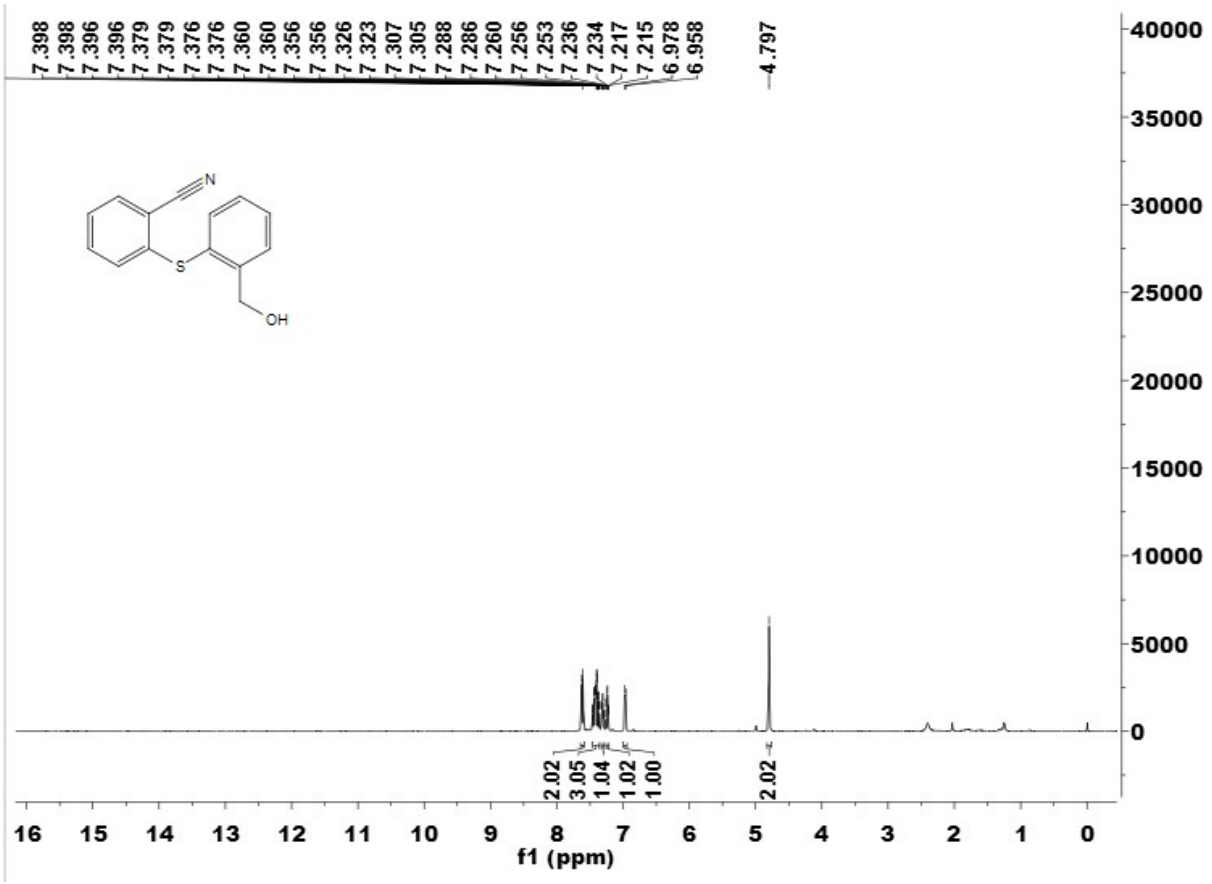


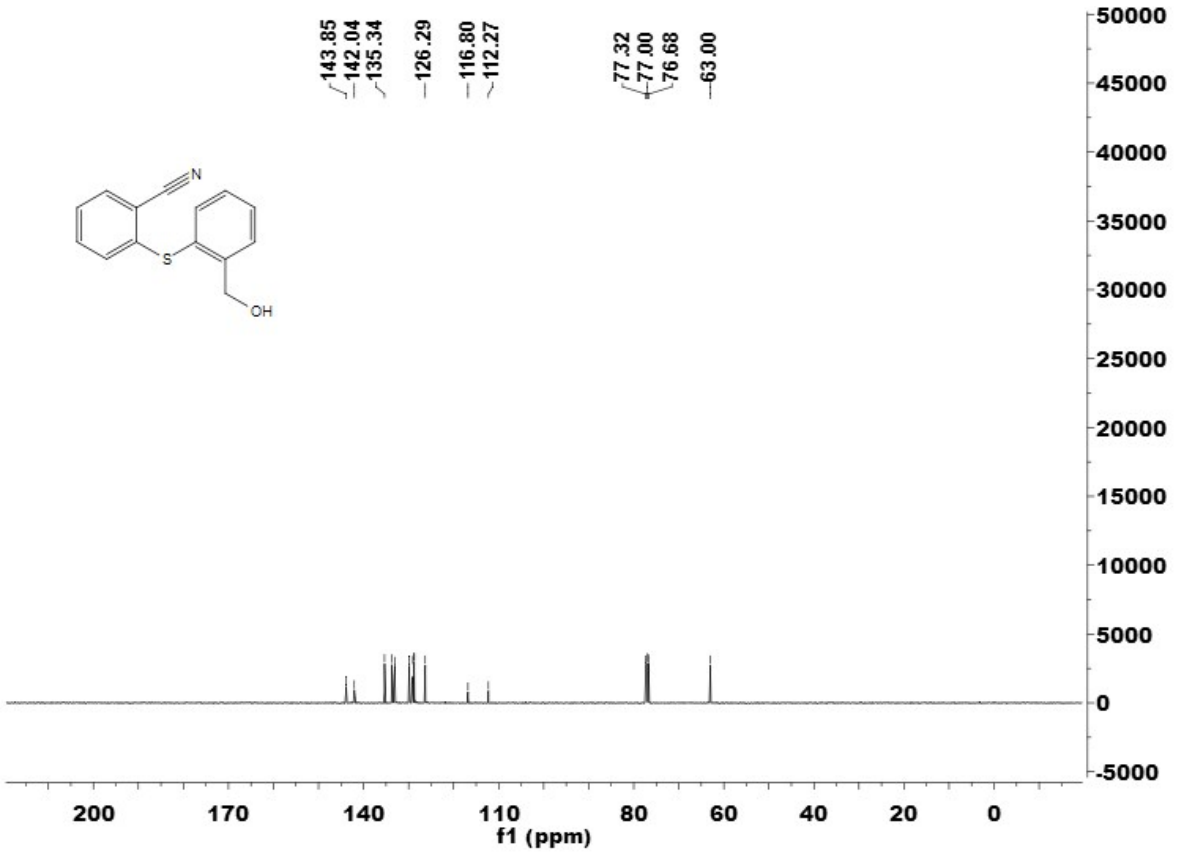
Dibenzo[b,d]thiophene-4-carbonitrile (9)



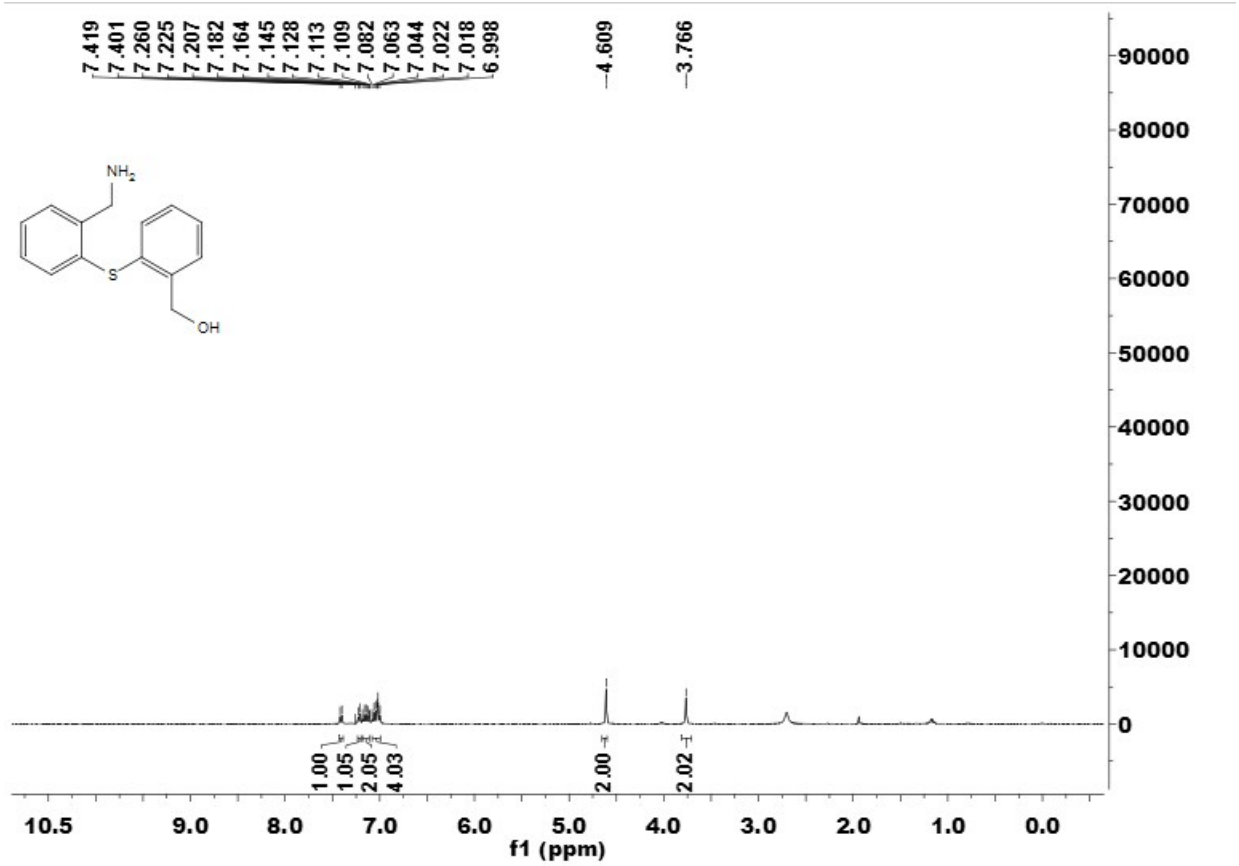


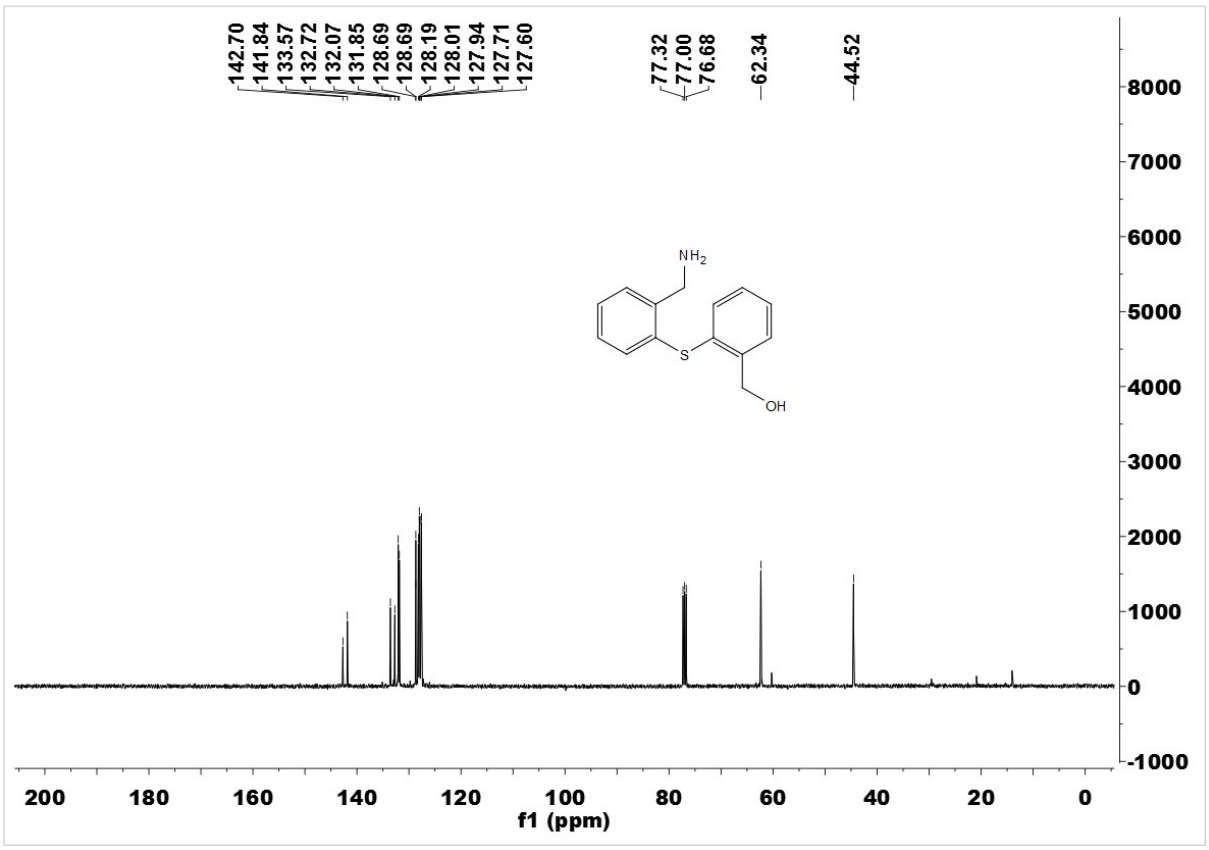
2-((2-(Hydroxymethyl)phenyl)thio)benzonitrile (3zf)



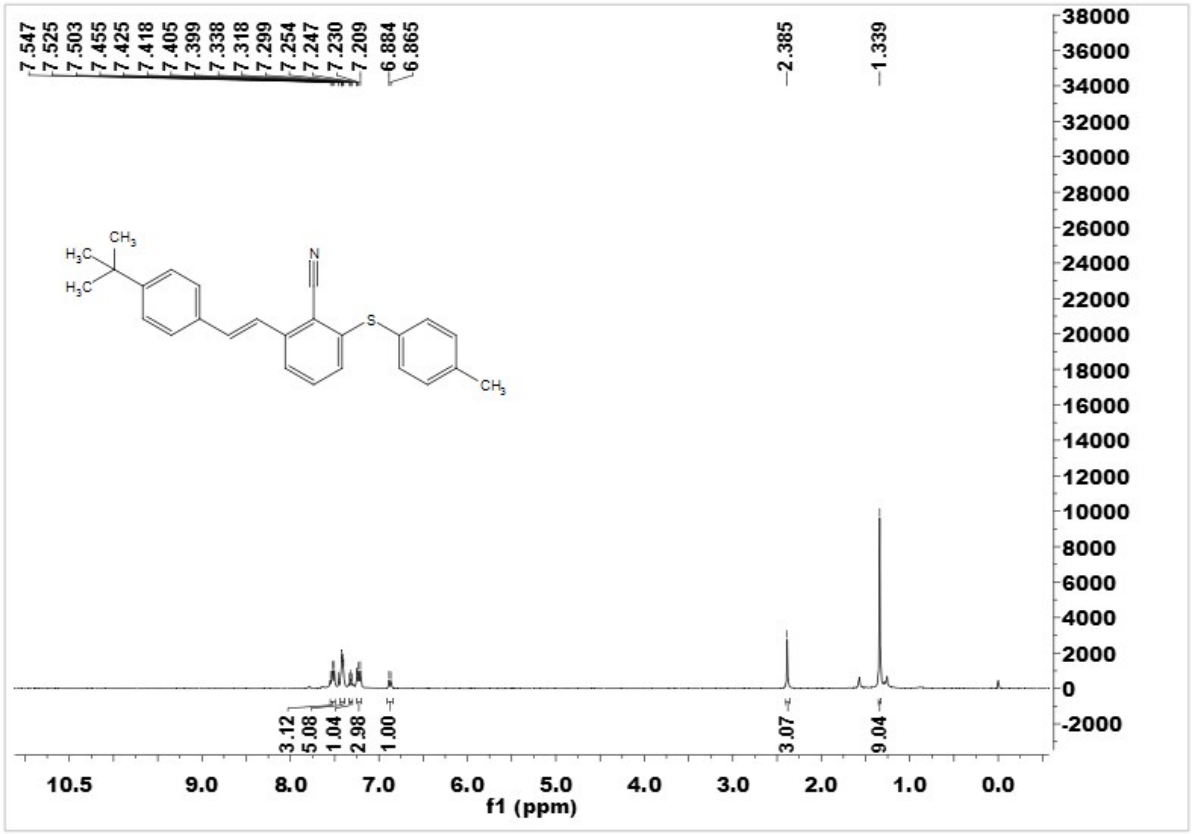


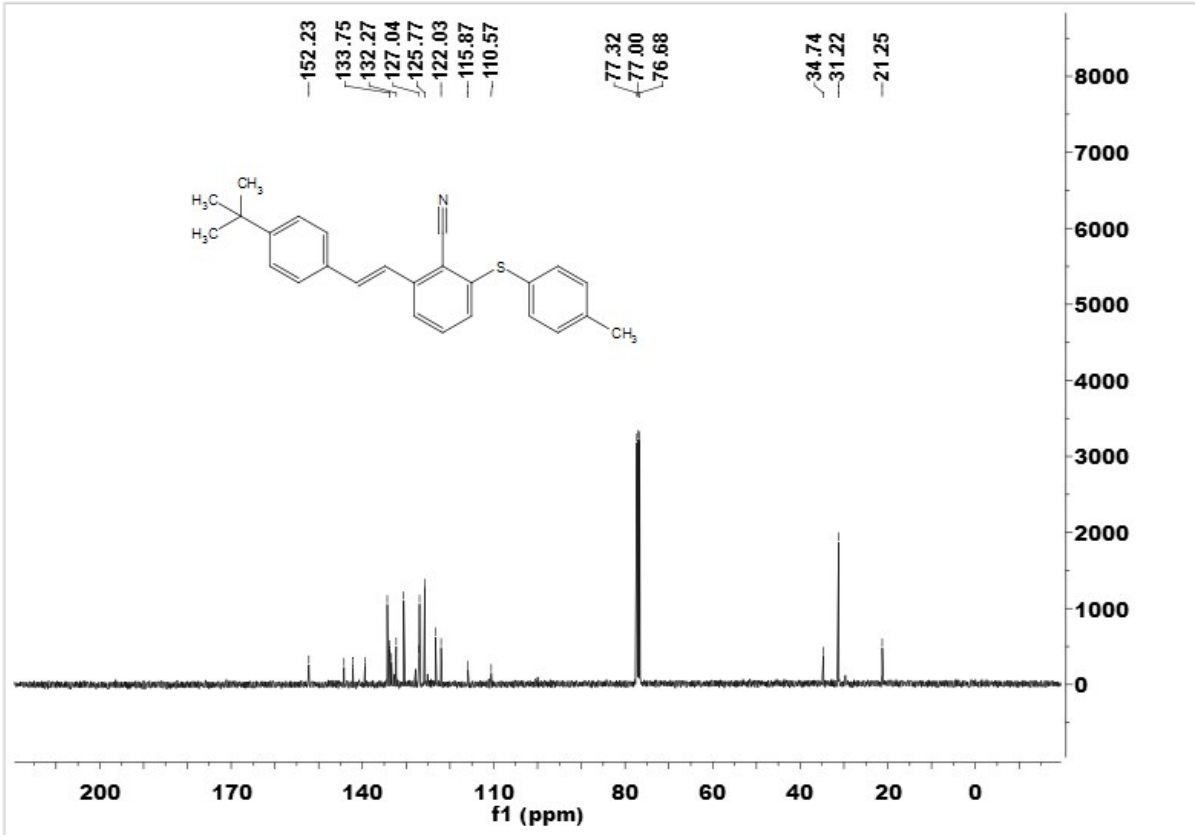
(2-((2-(Aminomethyl)phenyl)thio)phenyl)methanol (10)



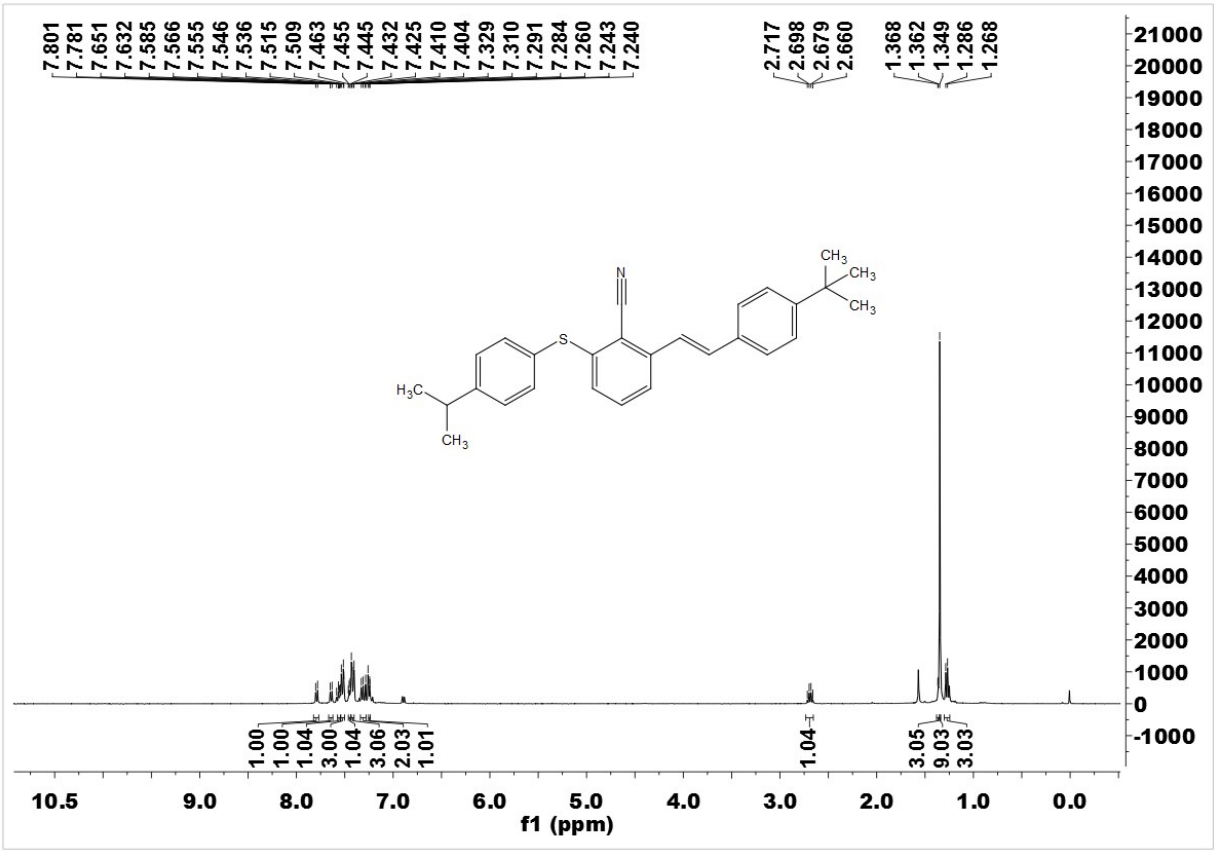


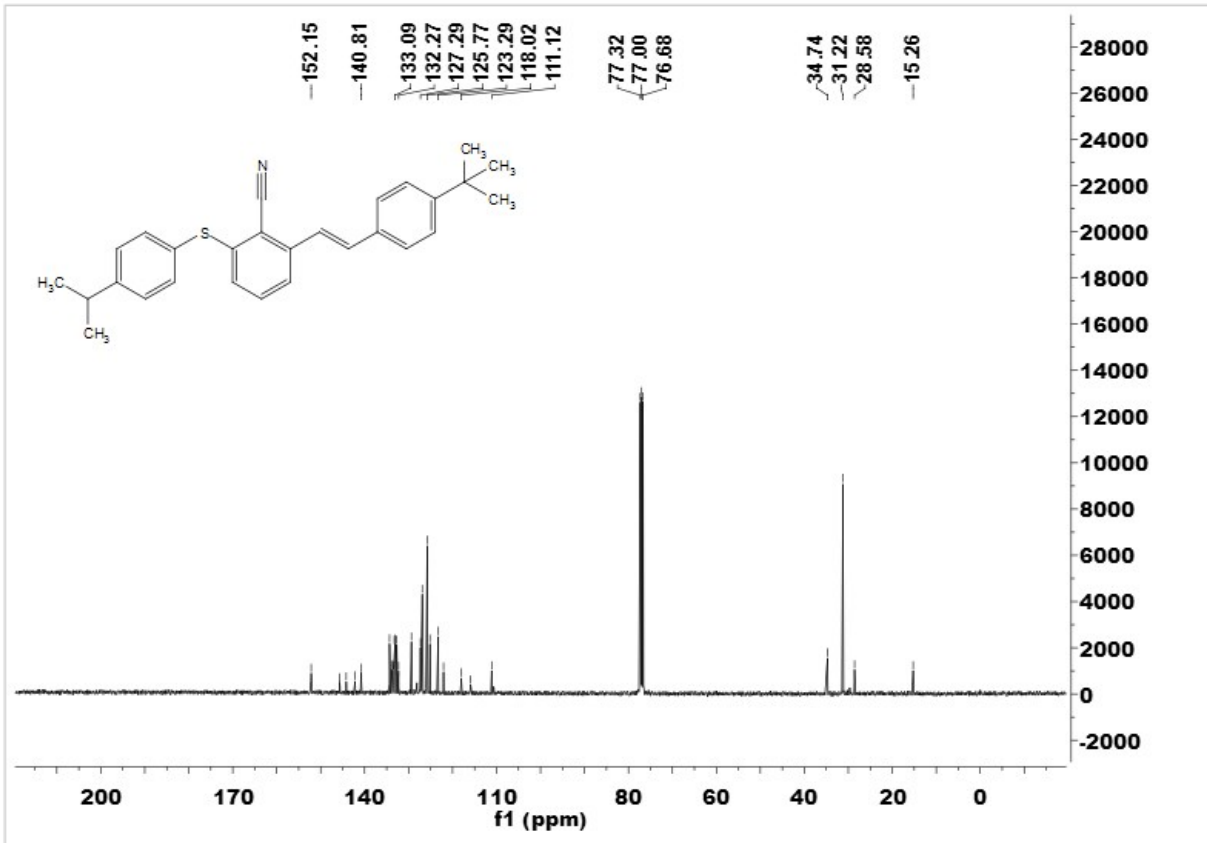
(*E*)-2-(4-(*tert*-Butyl)styryl)-6-(*p*-tolylthio)benzonitrile (12a)



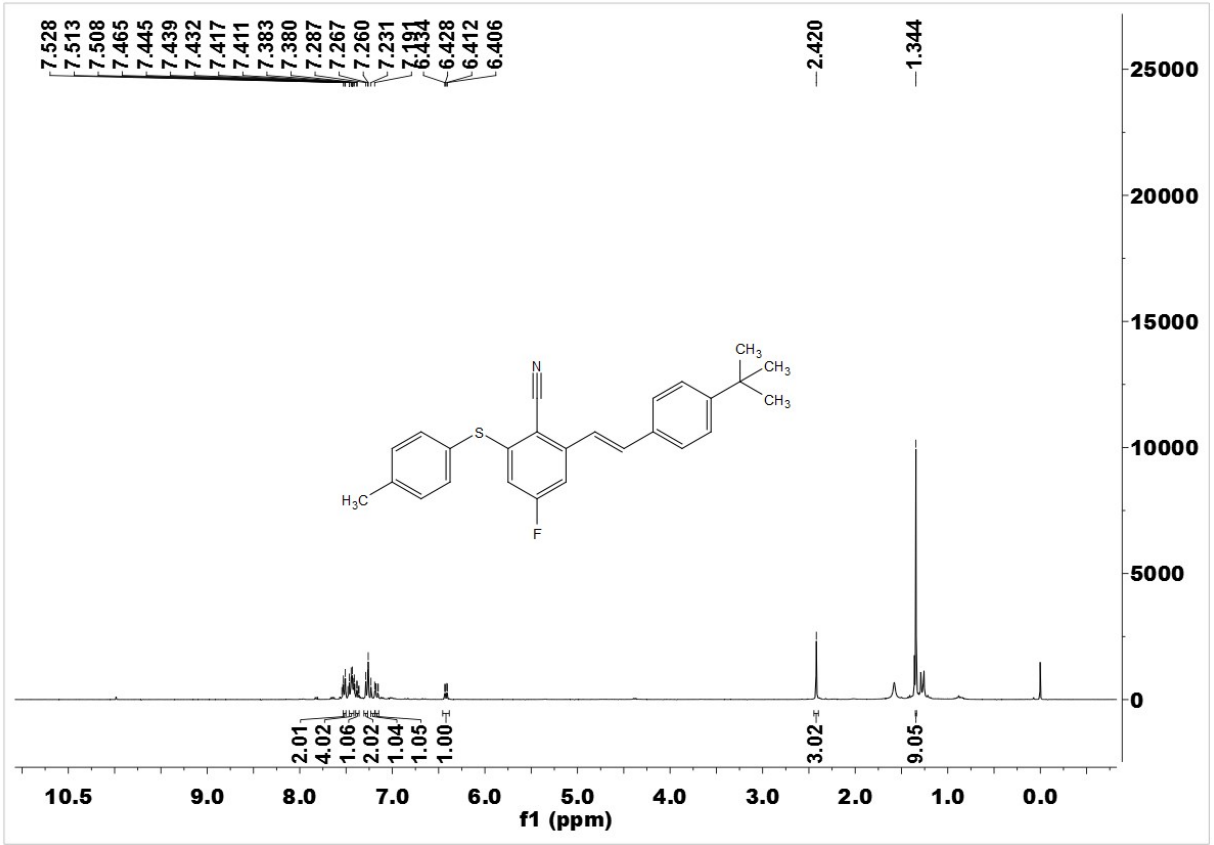


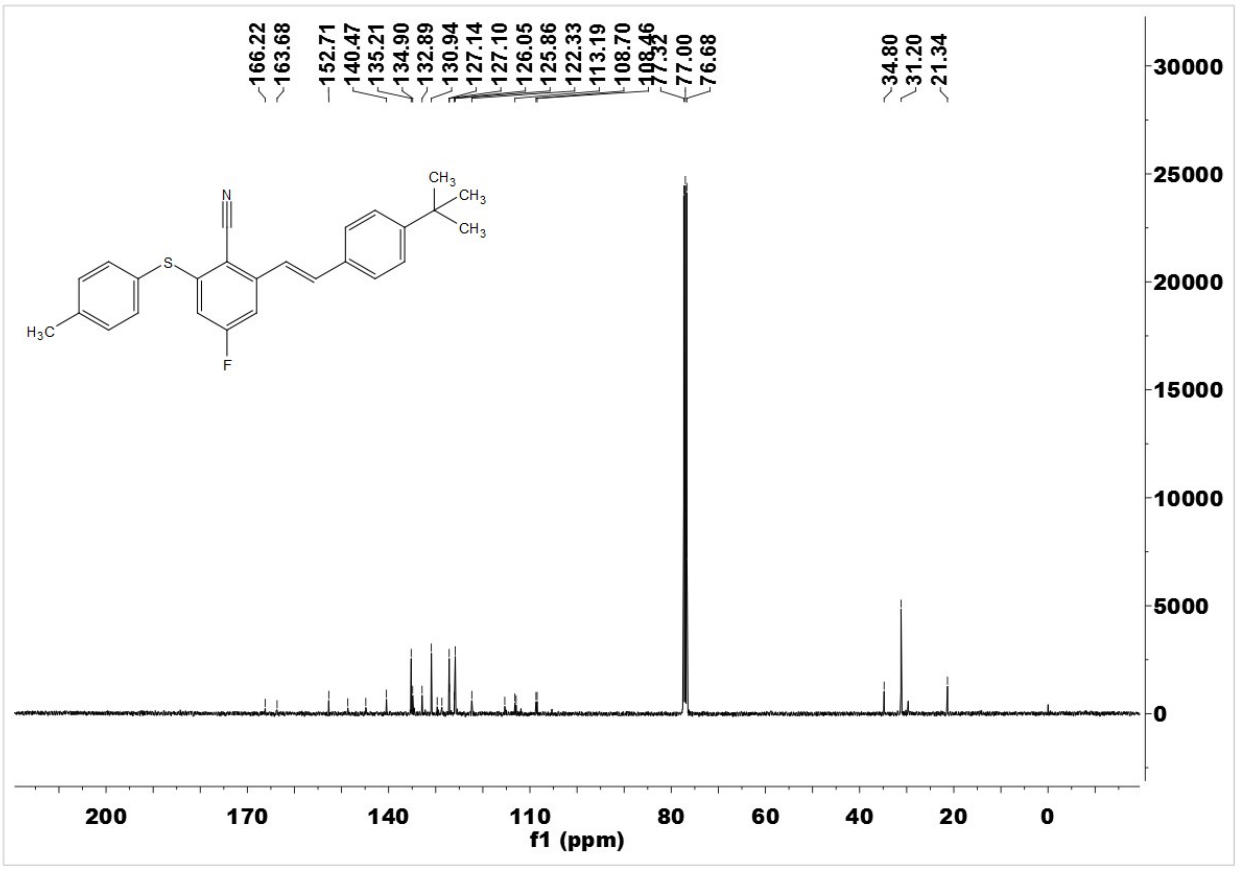
(*E*)-2-(4-(*tert*-Butyl)styryl)-6-((4-isopropylphenyl)thio)benzonitrile (12b)

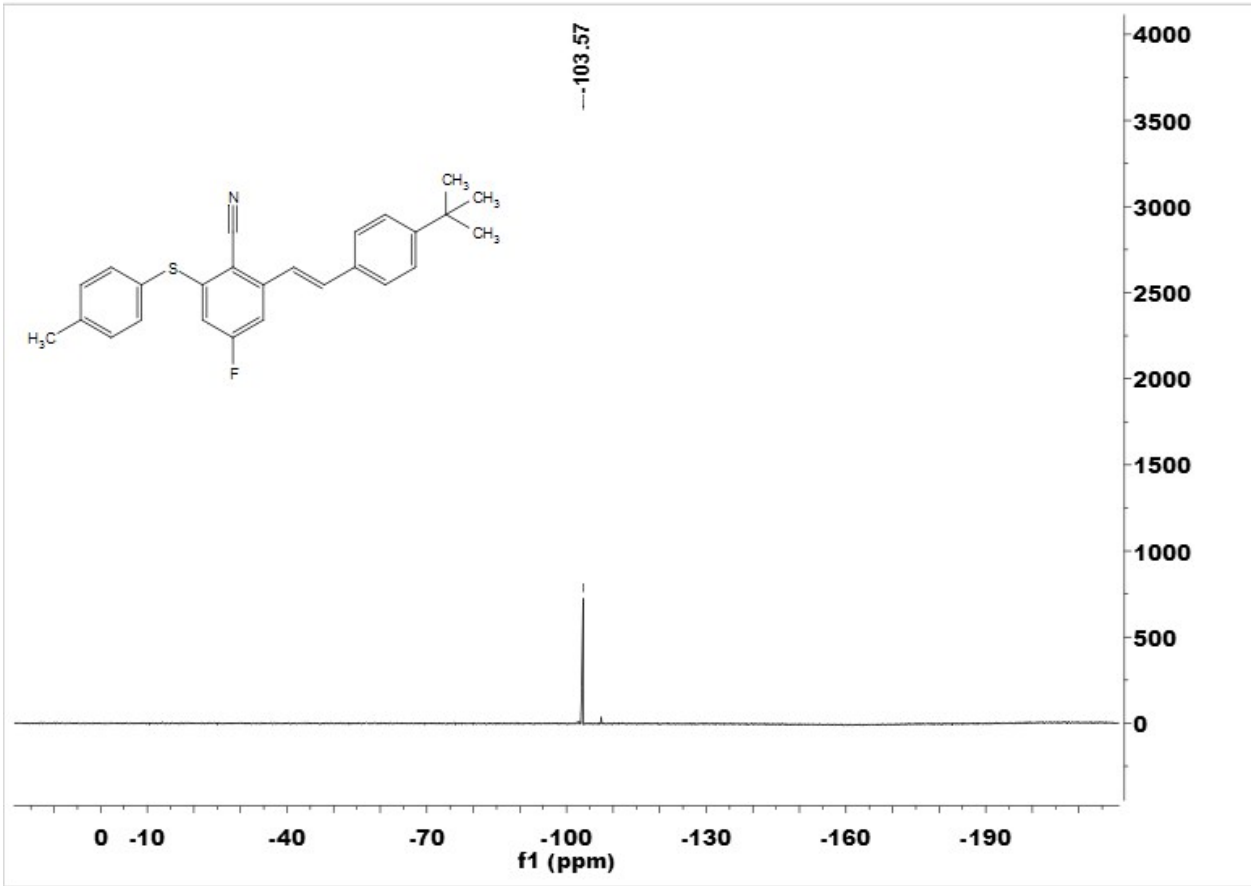




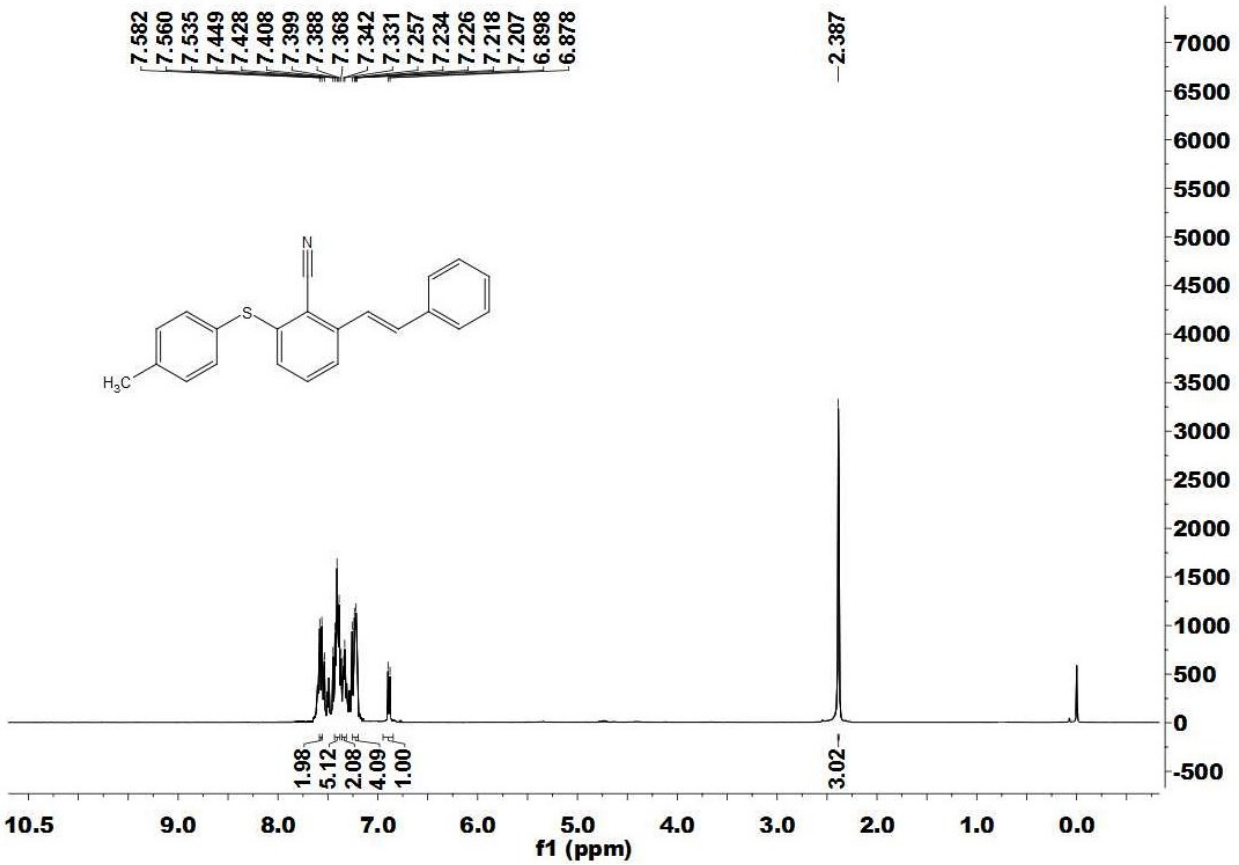
(*E*)-2-(4-(*tert*-Butyl)styryl)-4-fluoro-6-(*p*-tolylthio)benzonitrile (12c)

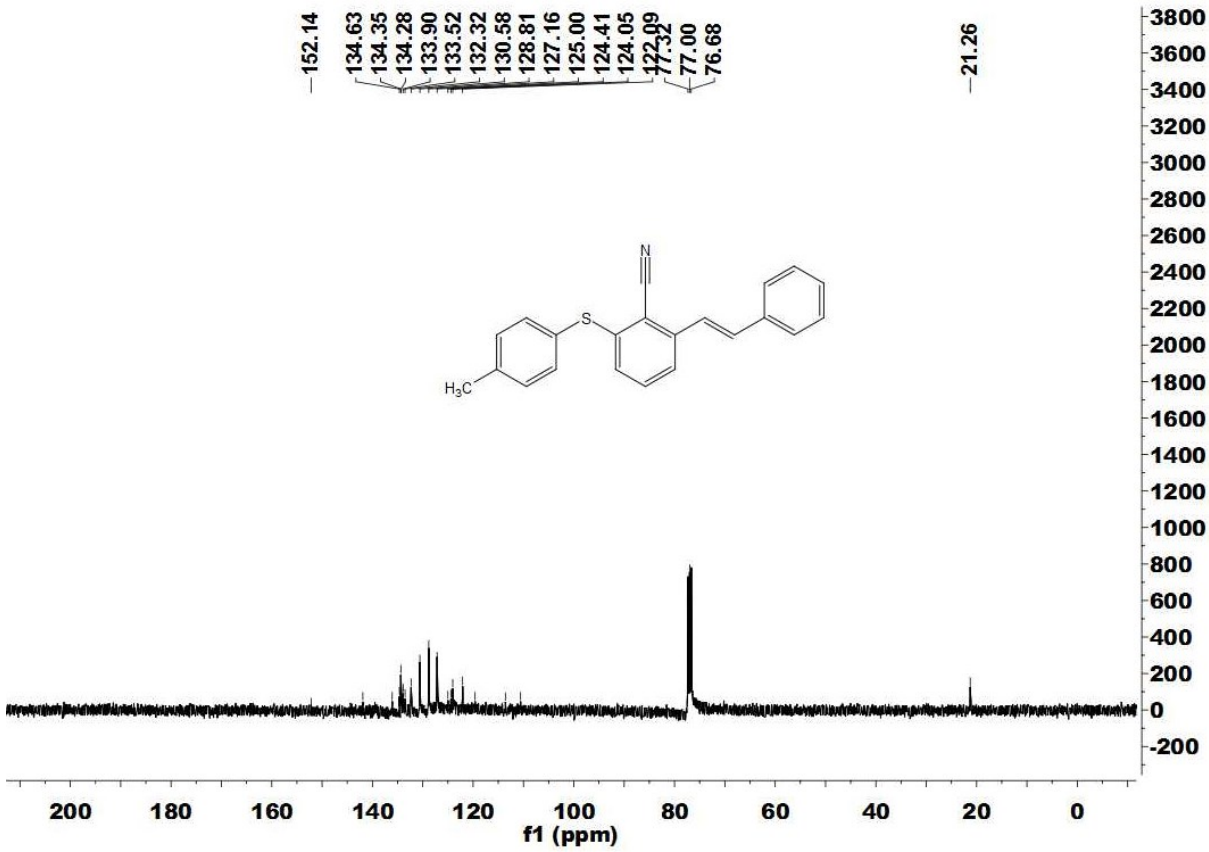



166.22
163.68
152.71
140.47
135.21
134.90
132.89
130.94
127.14
127.10
126.05
125.86
122.33
113.19
108.70
108.46
77.32
77.00
76.68
34.80
31.20
21.34
N
S
F
H3C
CH3
CH3
CH3
30000
25000
20000
15000
10000
5000
0
200
170
140
110
80
60
40
20
0
f1 (ppm)

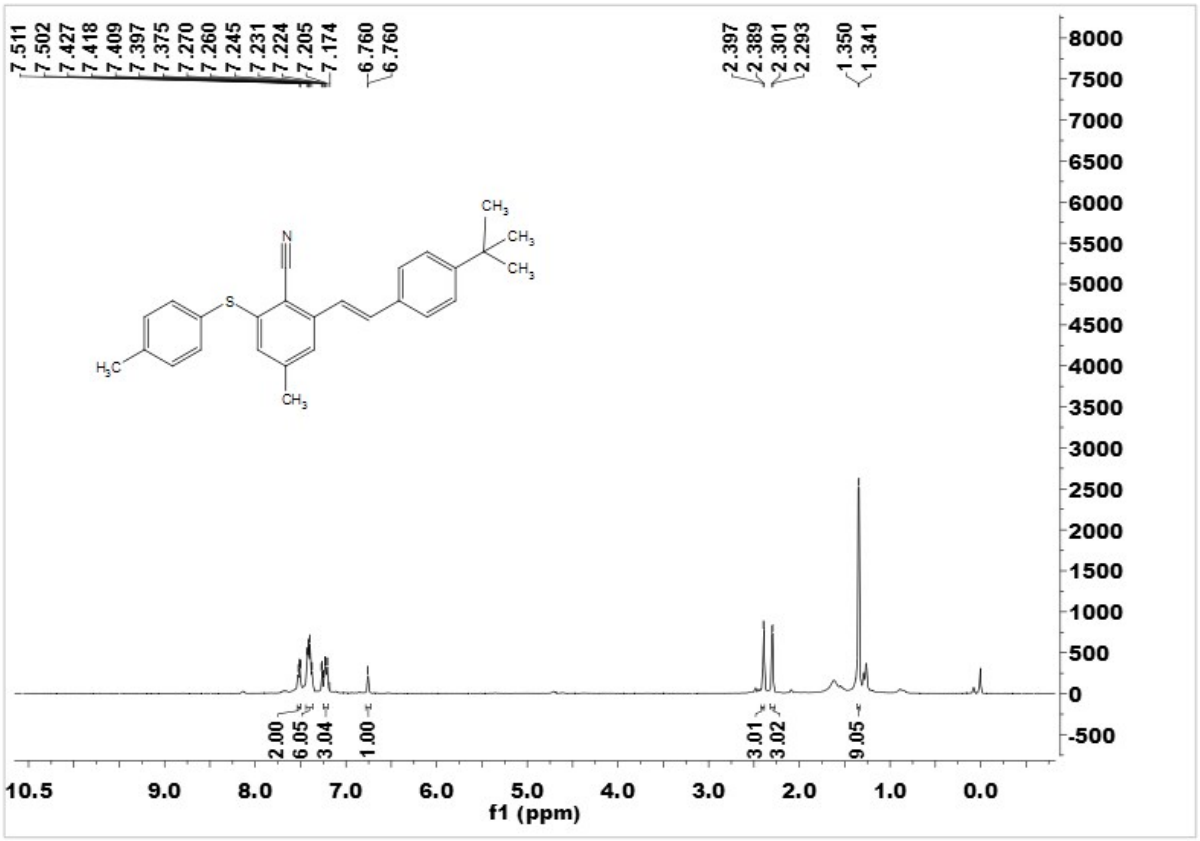

-103.57
N
S
F
H3C
CH3
CH3
CH3
4000
3500
3000
2500
2000
1500
1000
500
0
0
-10
-40
-70
-100
-130
-160
-190
f1 (ppm)

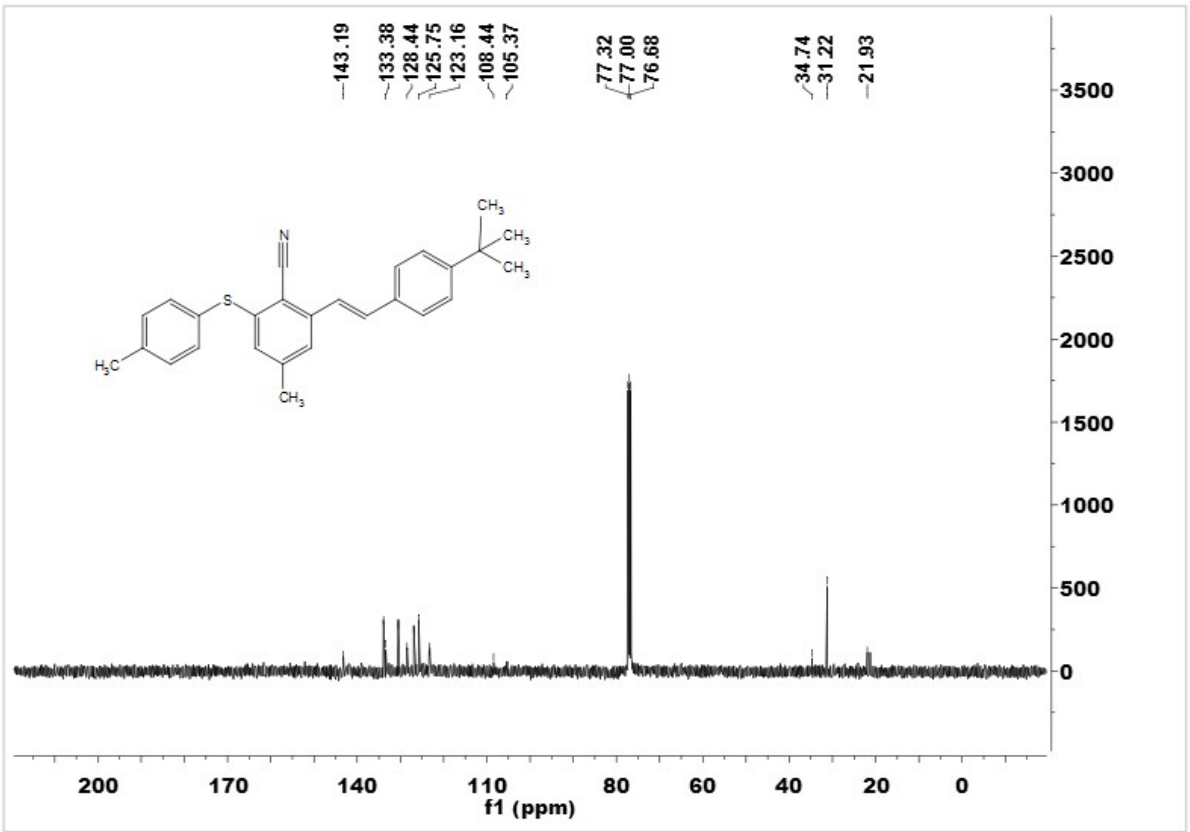
(*E*)-2-Styryl-6-(*p*-tolylthio)benzonitrile (12d)



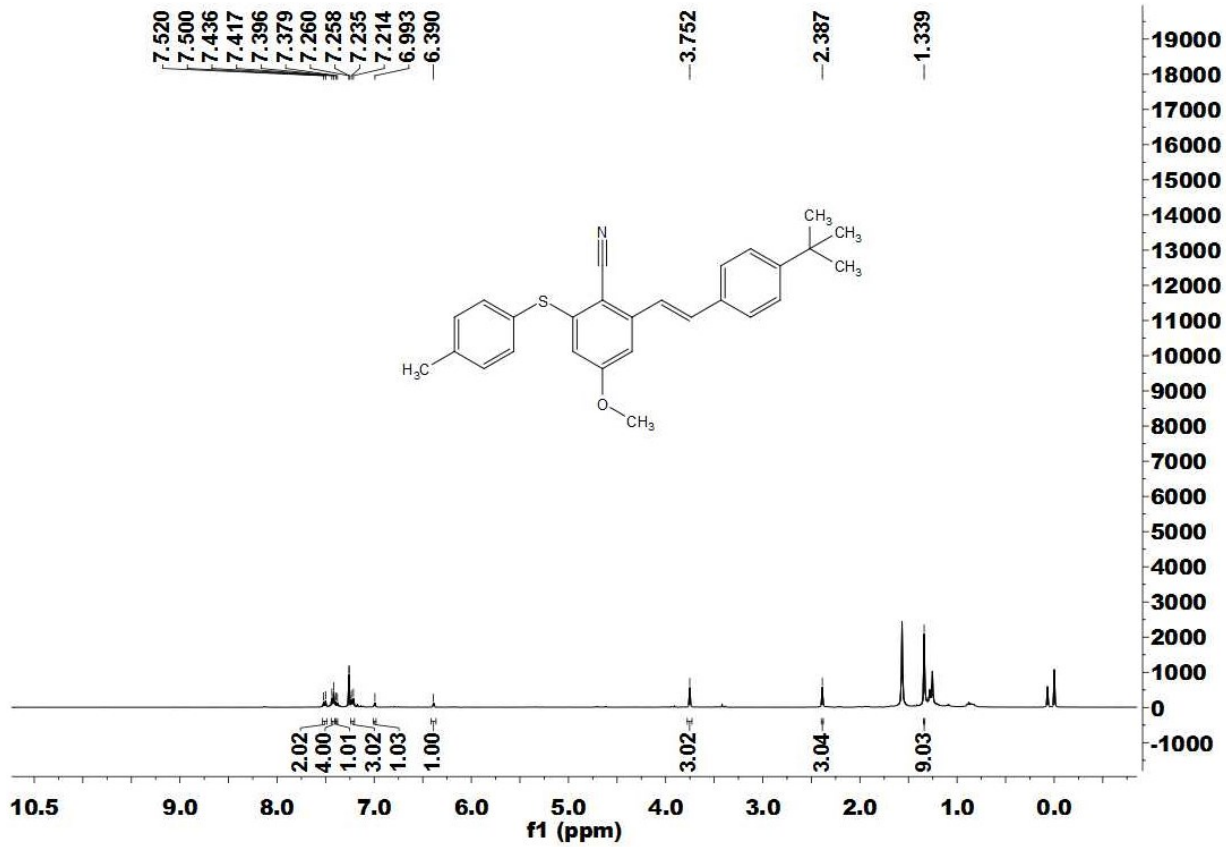


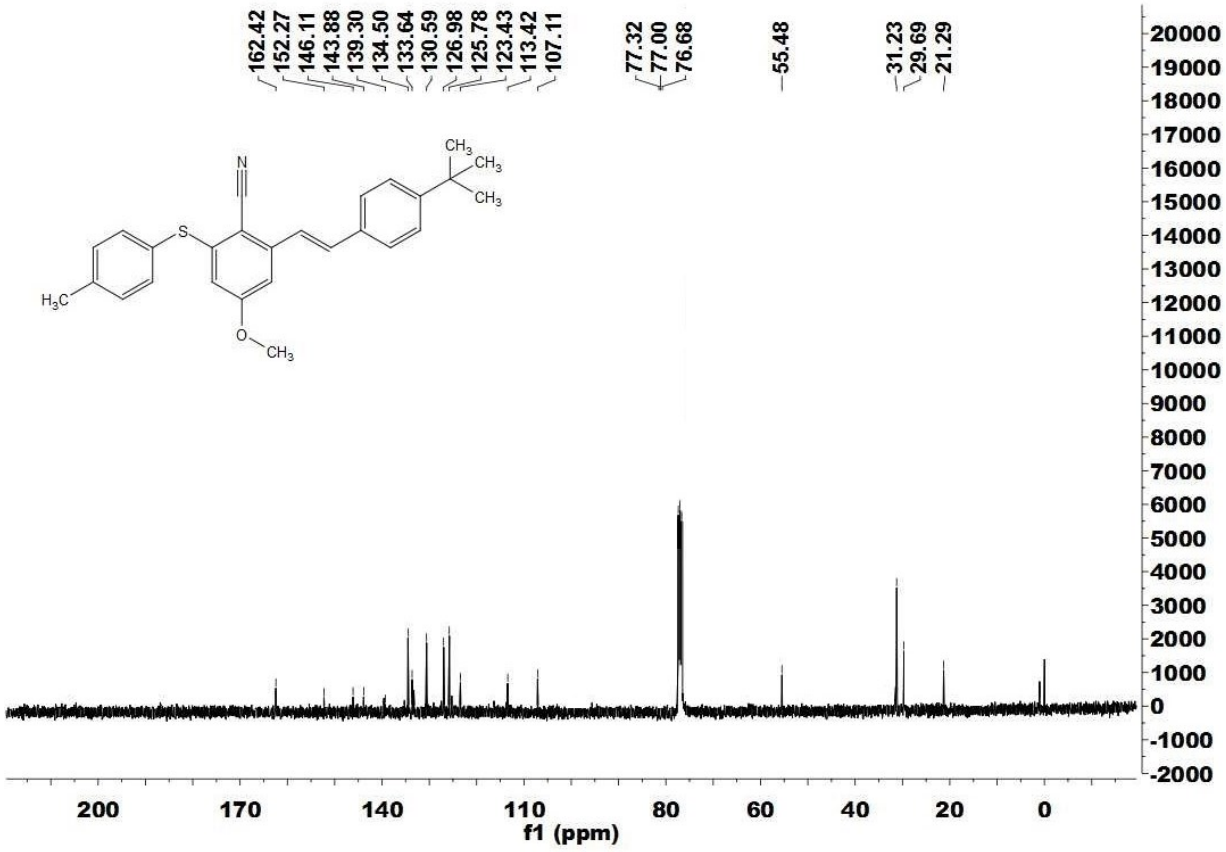
(*E*)-2-(4-(*tert*-Butyl)styryl)-4-methyl-6-(*p*-tolylthio)benzonitrile (12e)



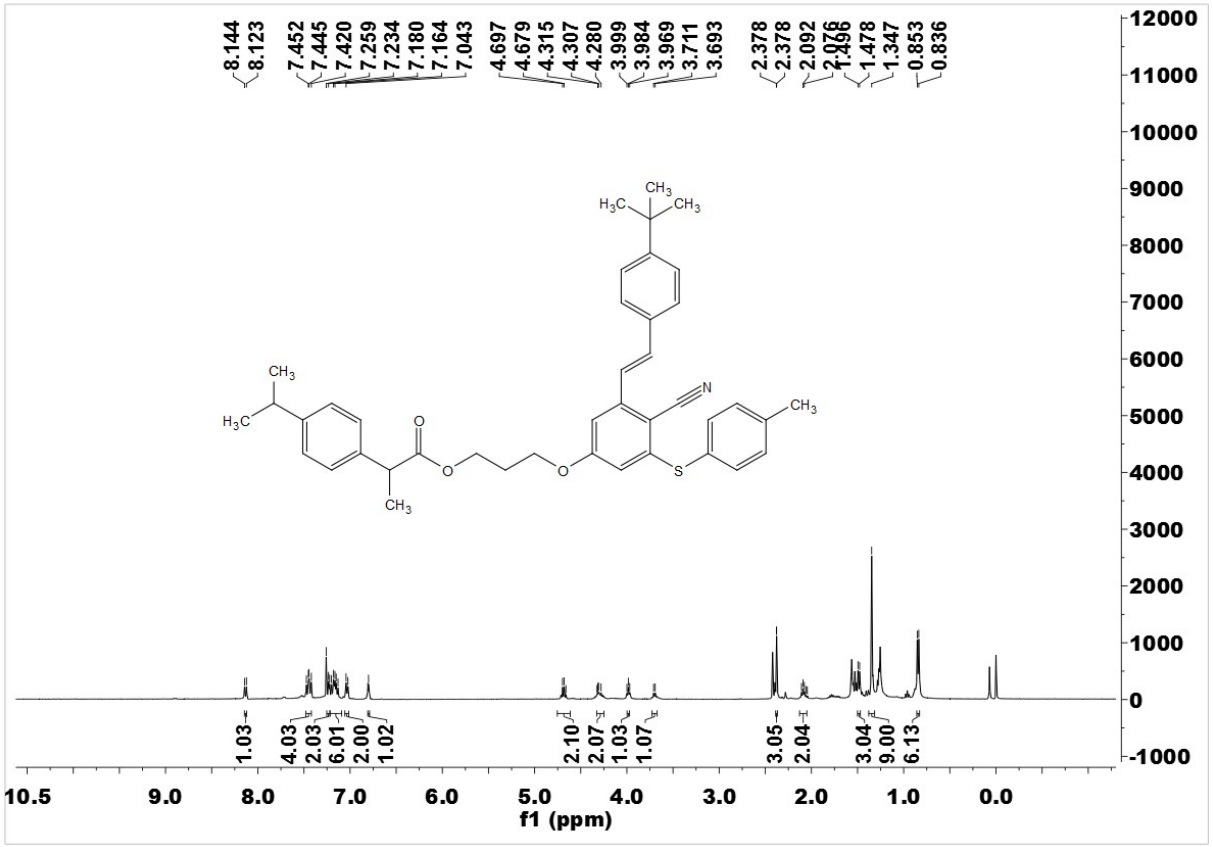


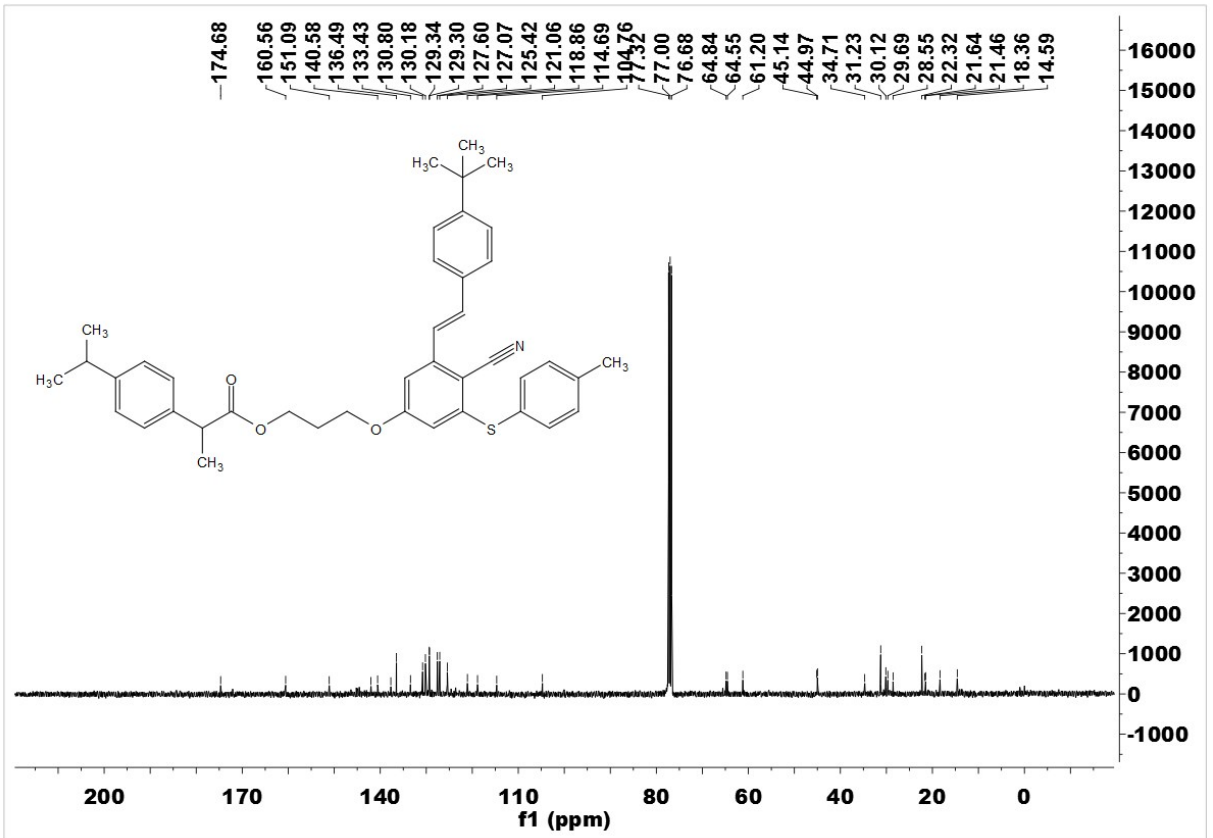
(*E*)-2-(4-(*tert*-Butyl)styryl)-4-methoxy-6-(*p*-tolylthio)benzonitrile (12f)



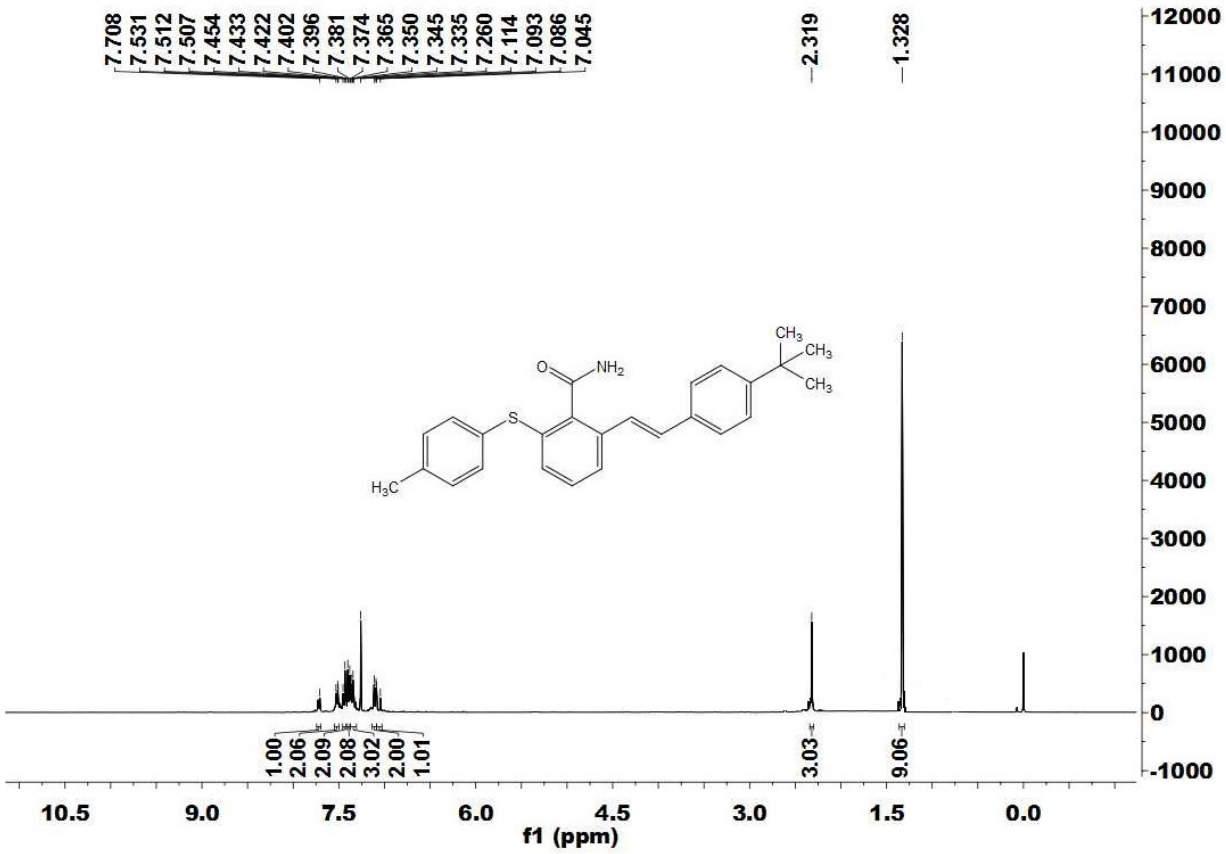


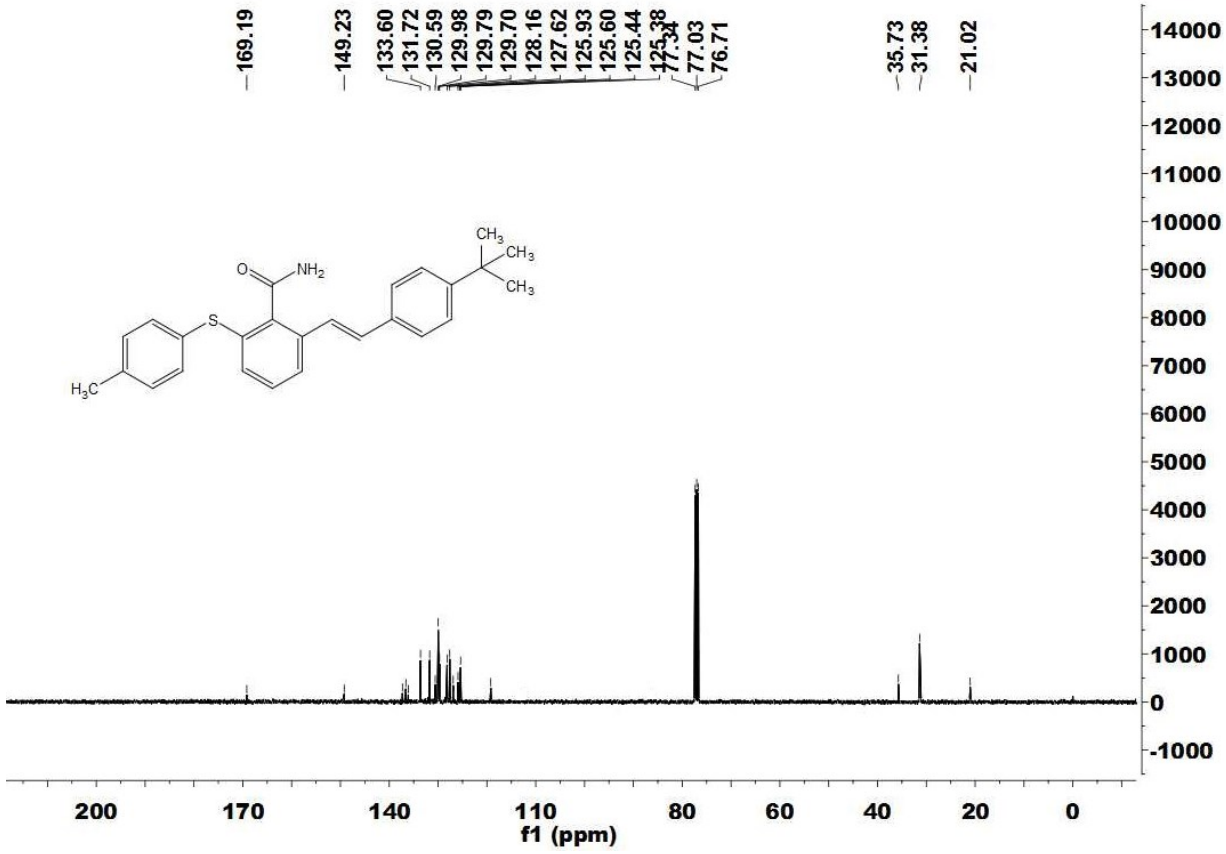
(*E*)-3-(3-(4-(*tert*-Butyl)styryl)-4-cyano-5-(*p*-tolylthio)phenoxy)propyl 2-(4-isopropylphenyl) propanoate (12g)



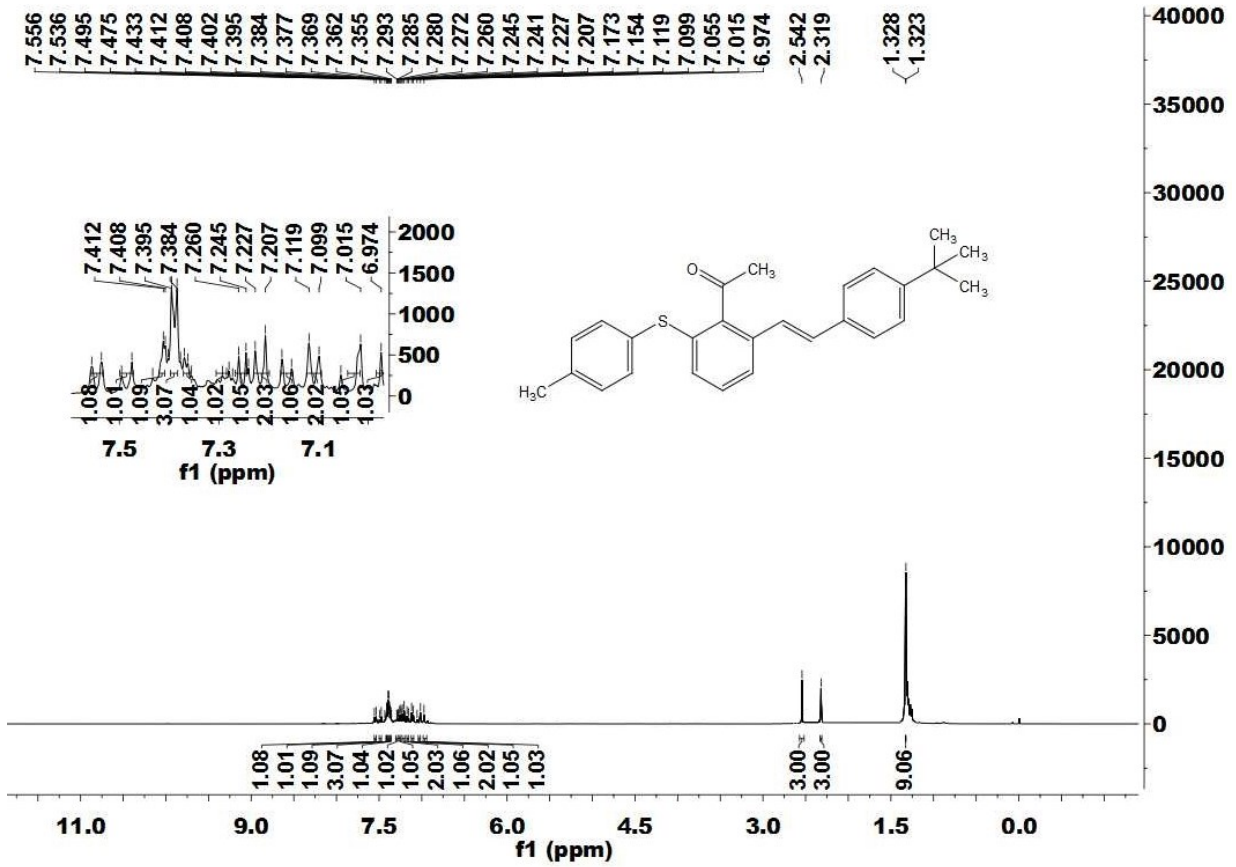


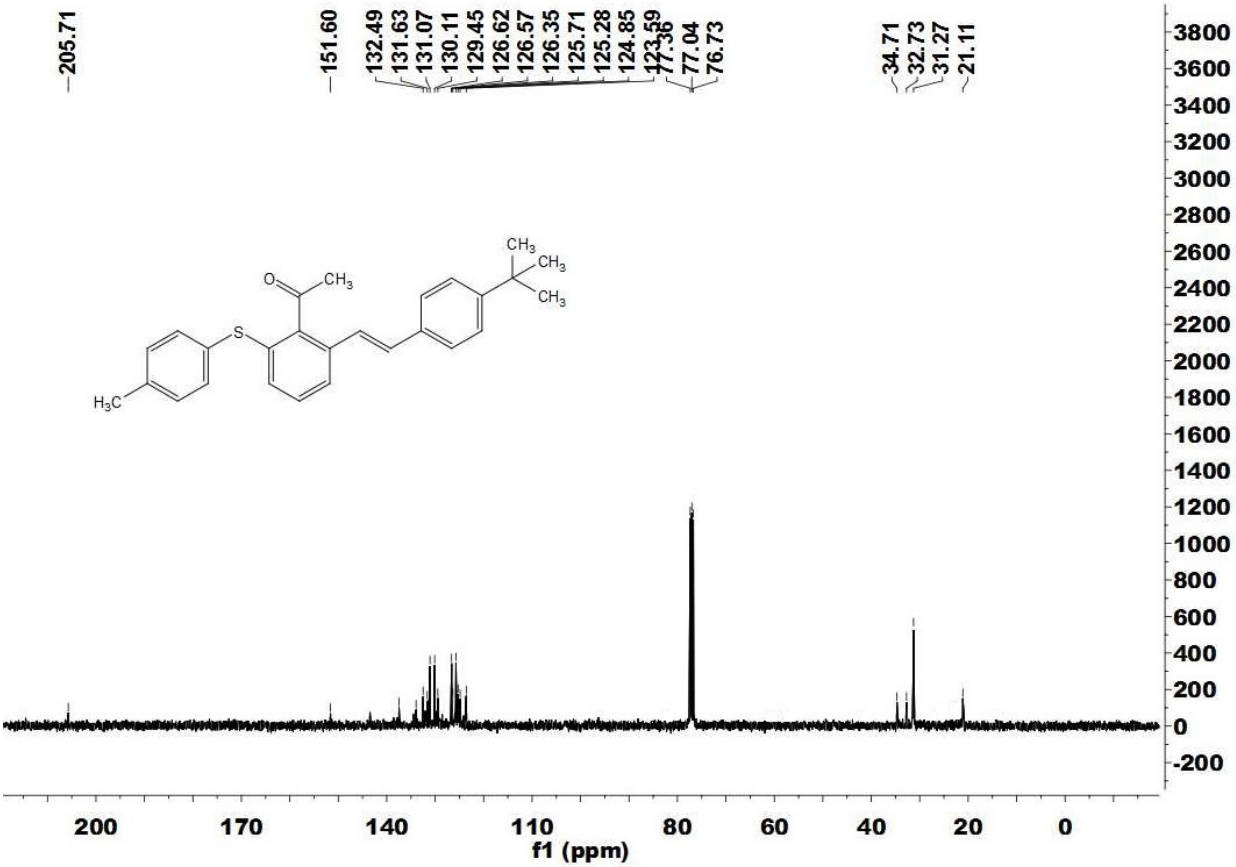
(*E*)-2-(4-(*tert*-Butyl)styryl)-6-(*p*-tolylthio)benzamide (12a-1)



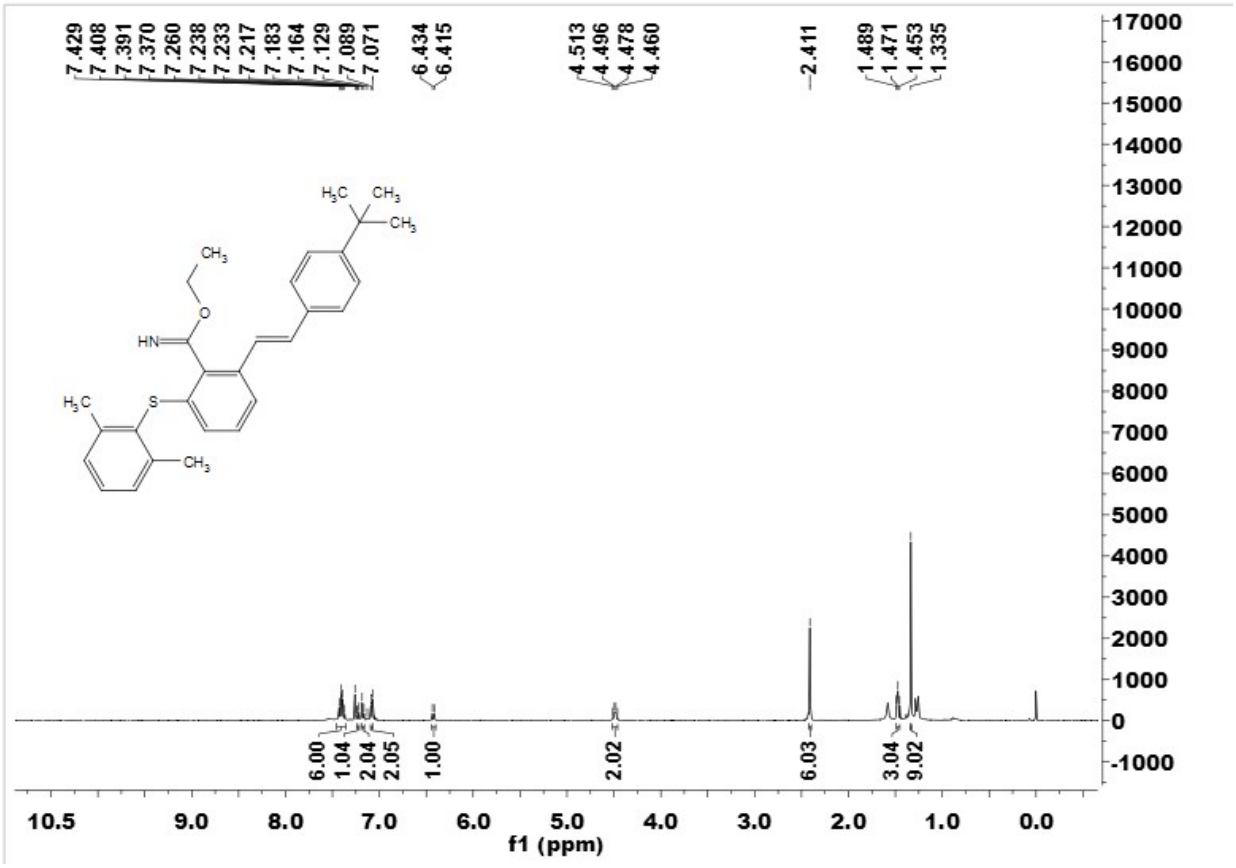


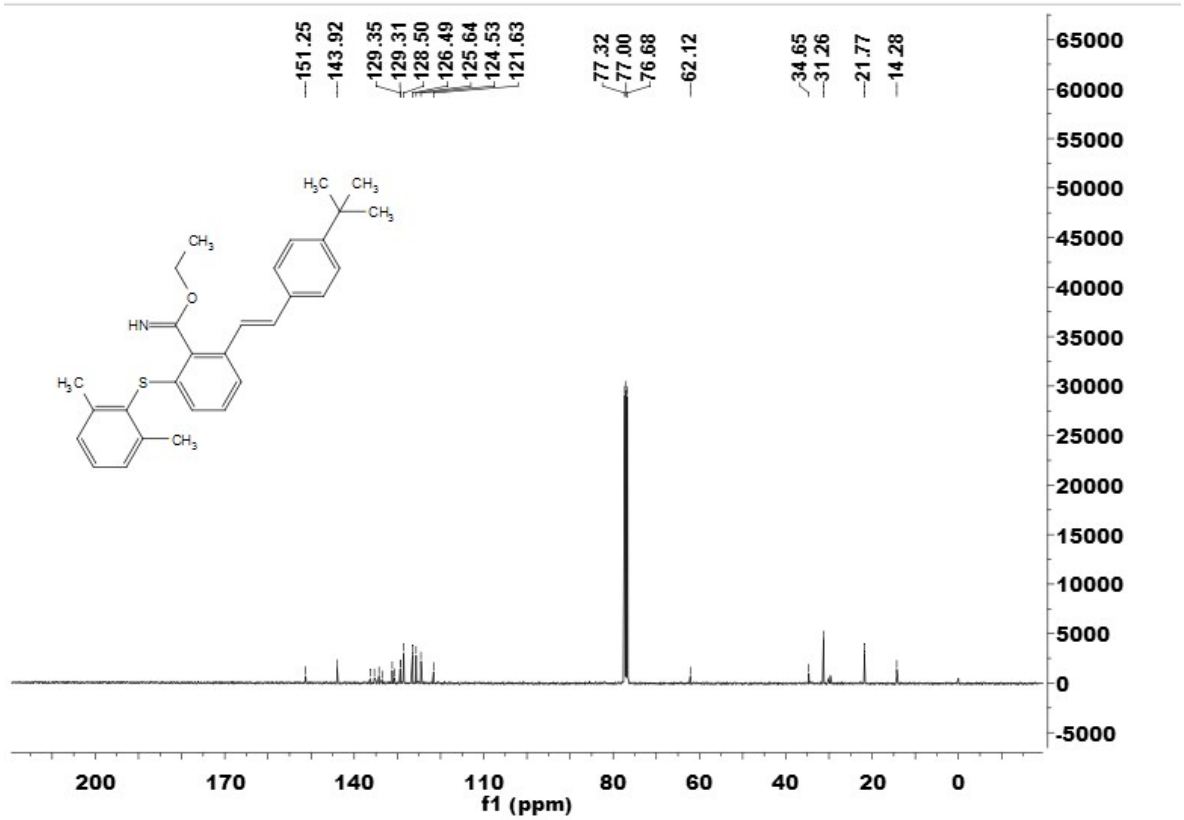
(*E*)-1-(2-(4-(*tert*-Butyl)styryl)-6-(*p*-tolylthio)phenyl)ethan-1-one (12a-2)



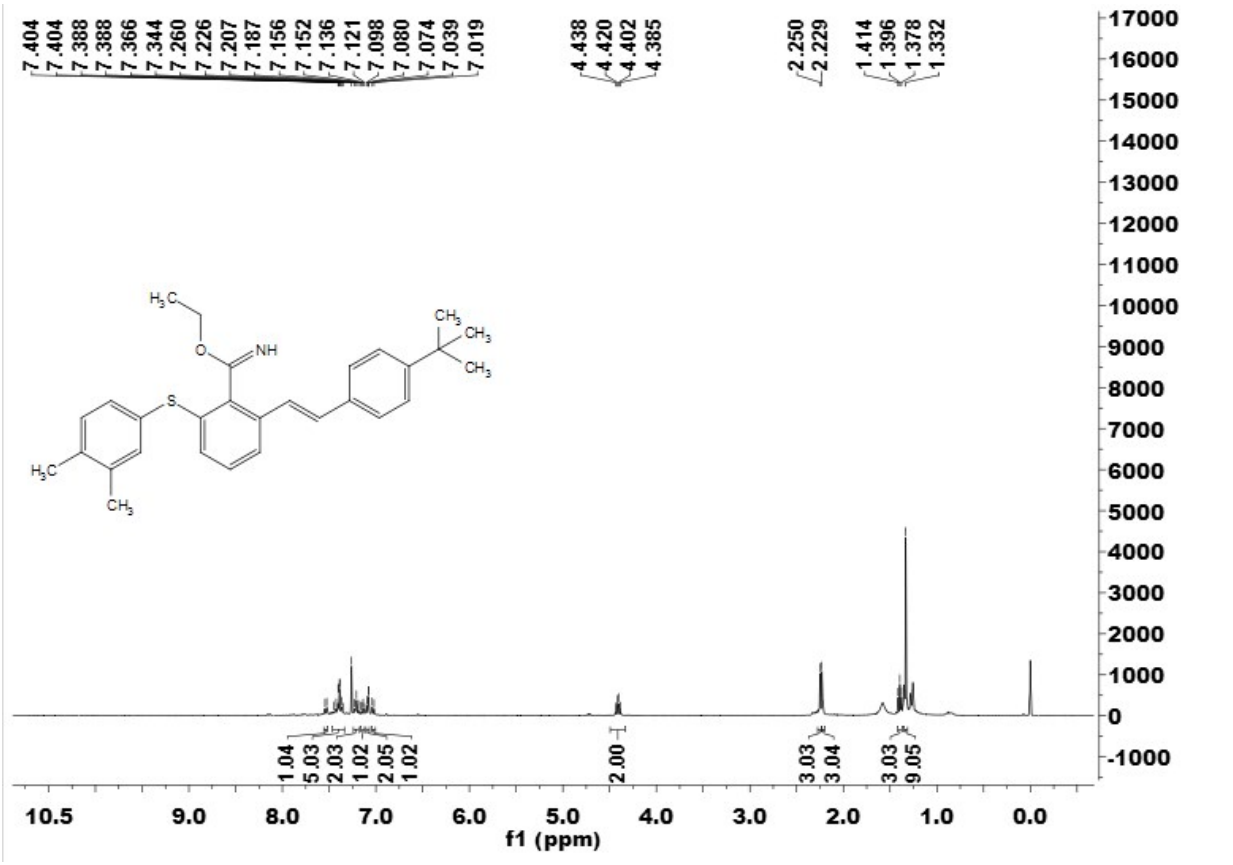


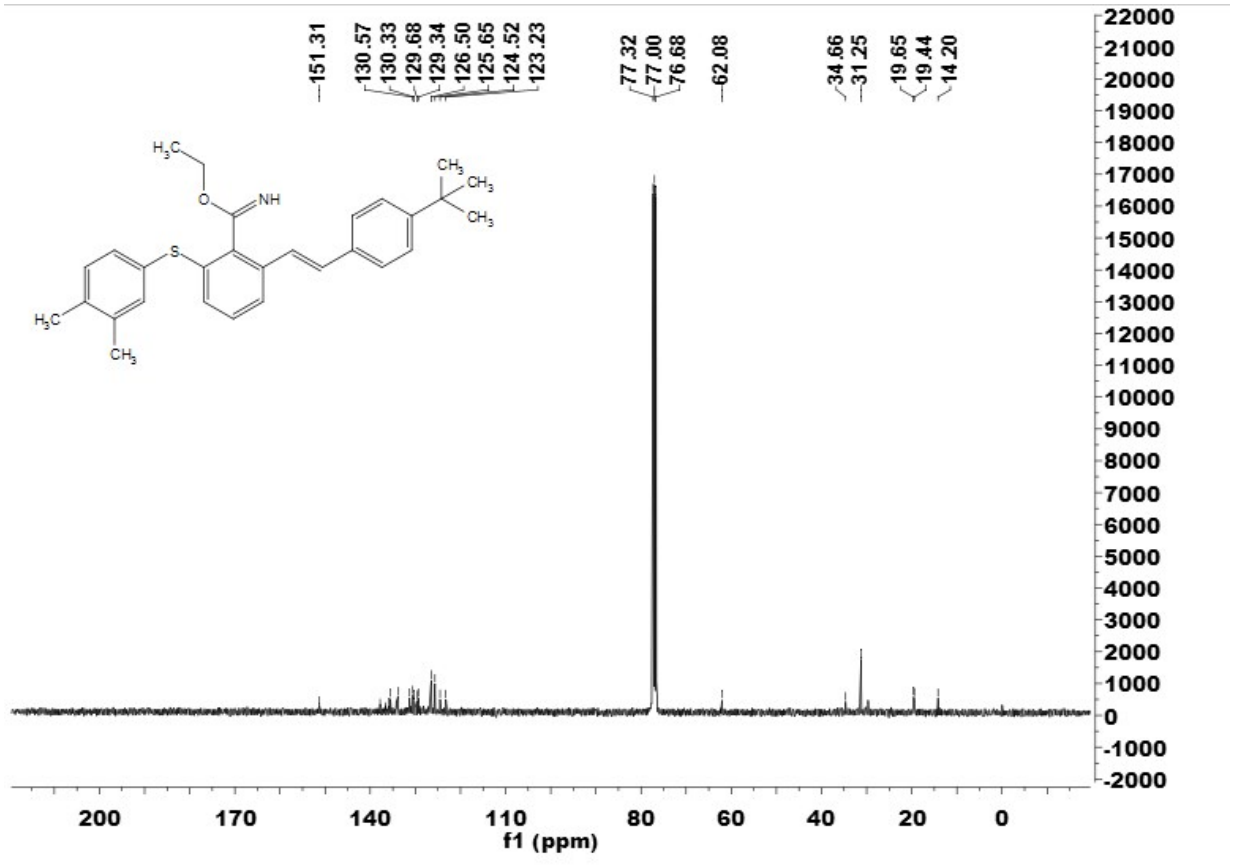
Ethyl (*E*)-2-(4-(*tert*-butyl)styryl)-6-((2,6-dimethylphenyl)thio)benzimidate (14a)



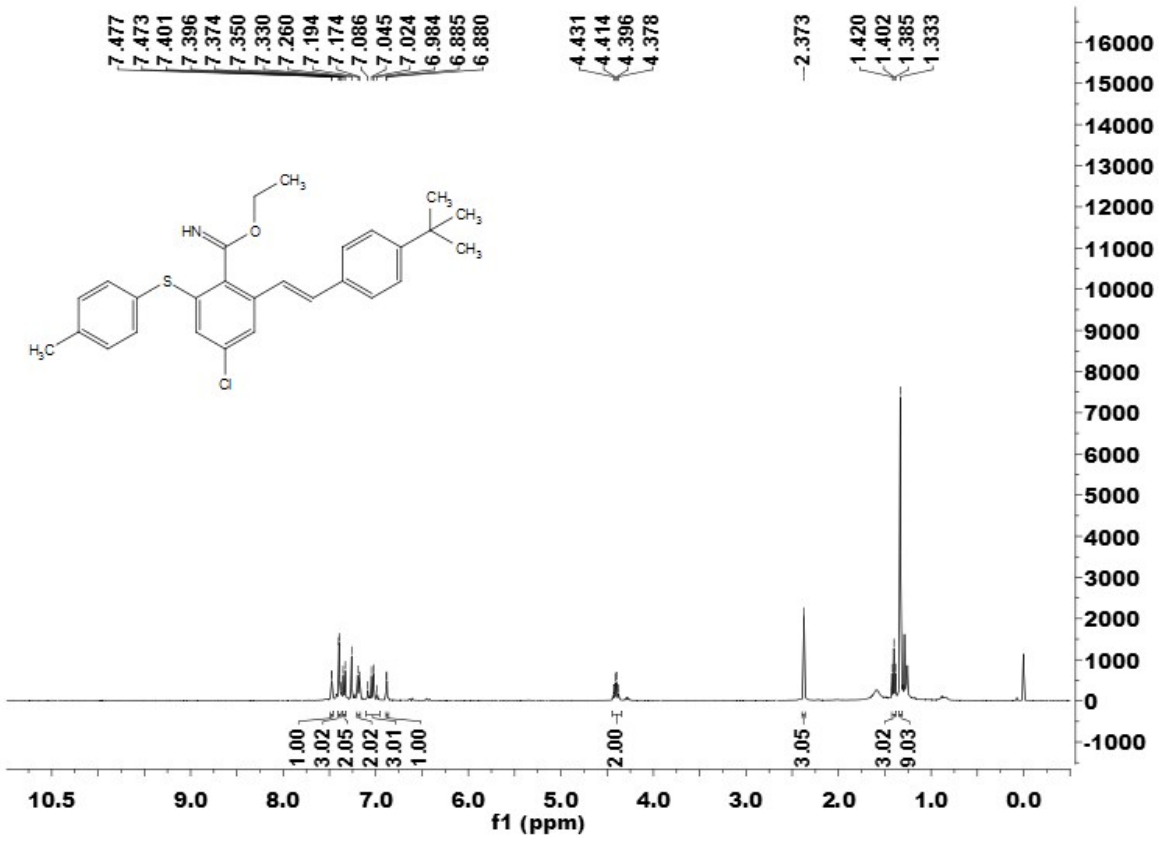


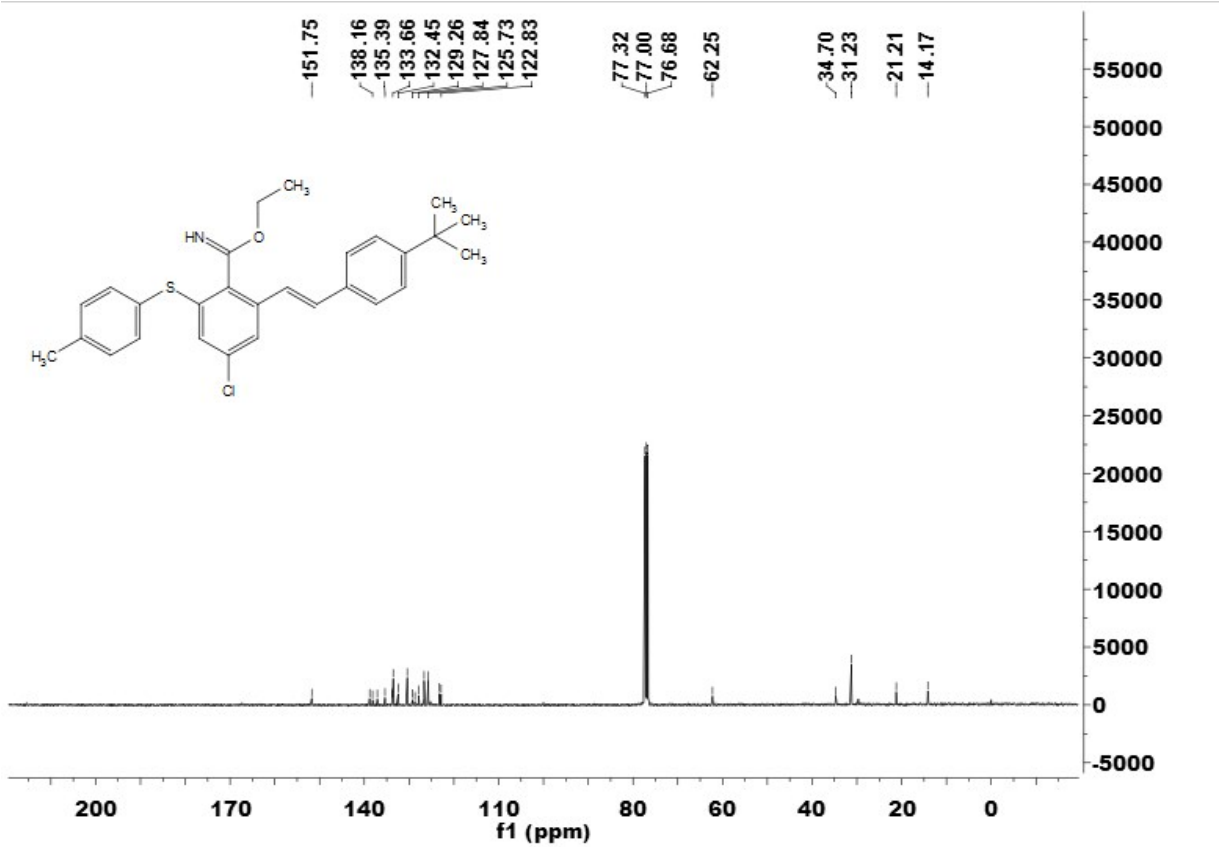
Ethyl (*E*)-2-(4-(*tert*-butyl)styryl)-6-((3,4-dimethylphenyl)thio)benzimidate (14b)



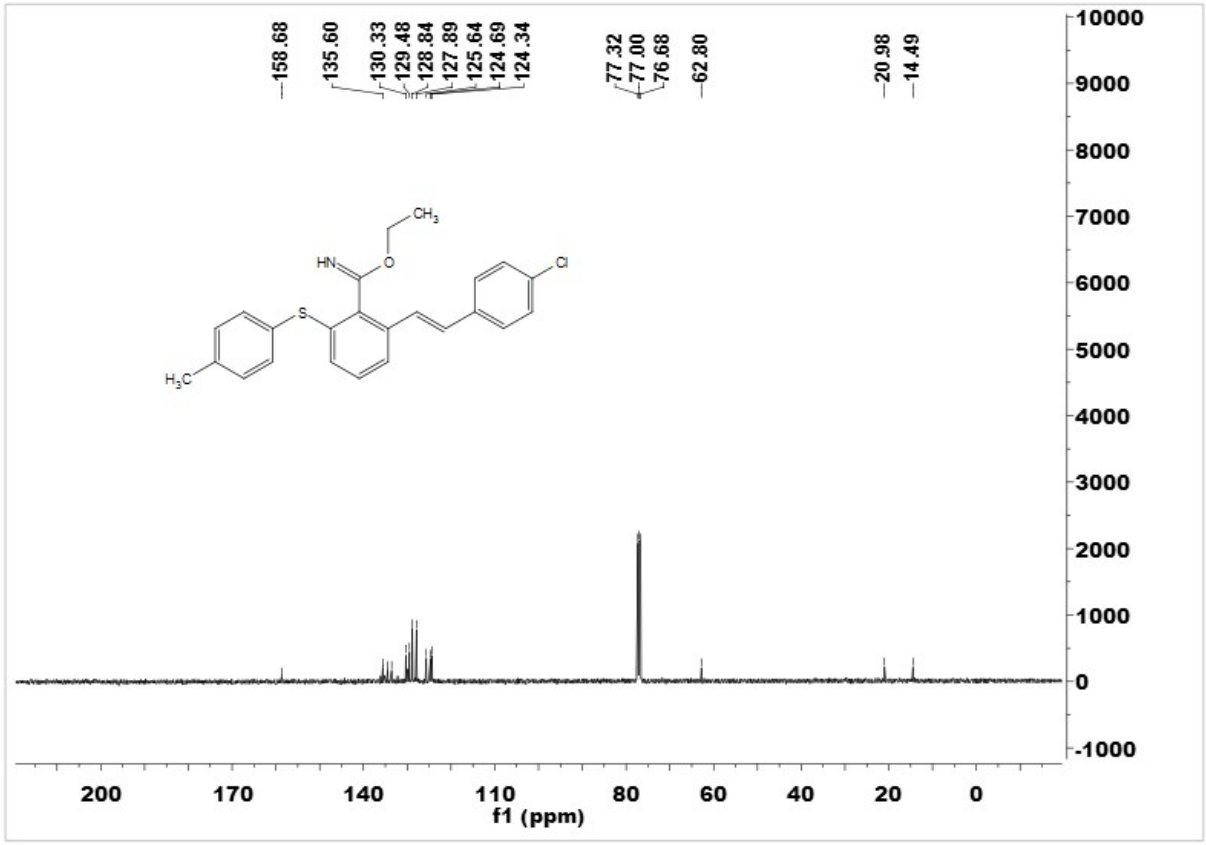


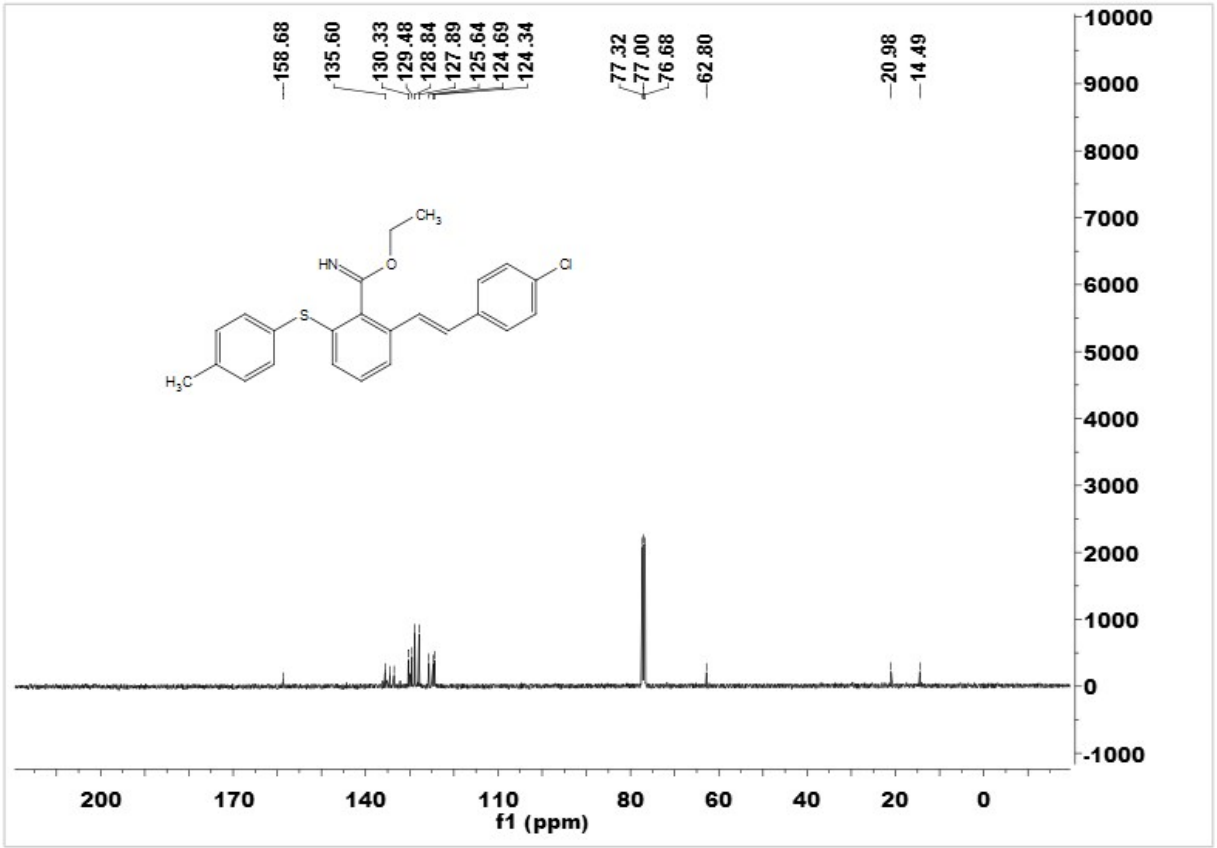
Ethyl (*E*)-2-(3,4-dimethylstyryl)-6-(*p*-tolylthio)benzimidate (14c)



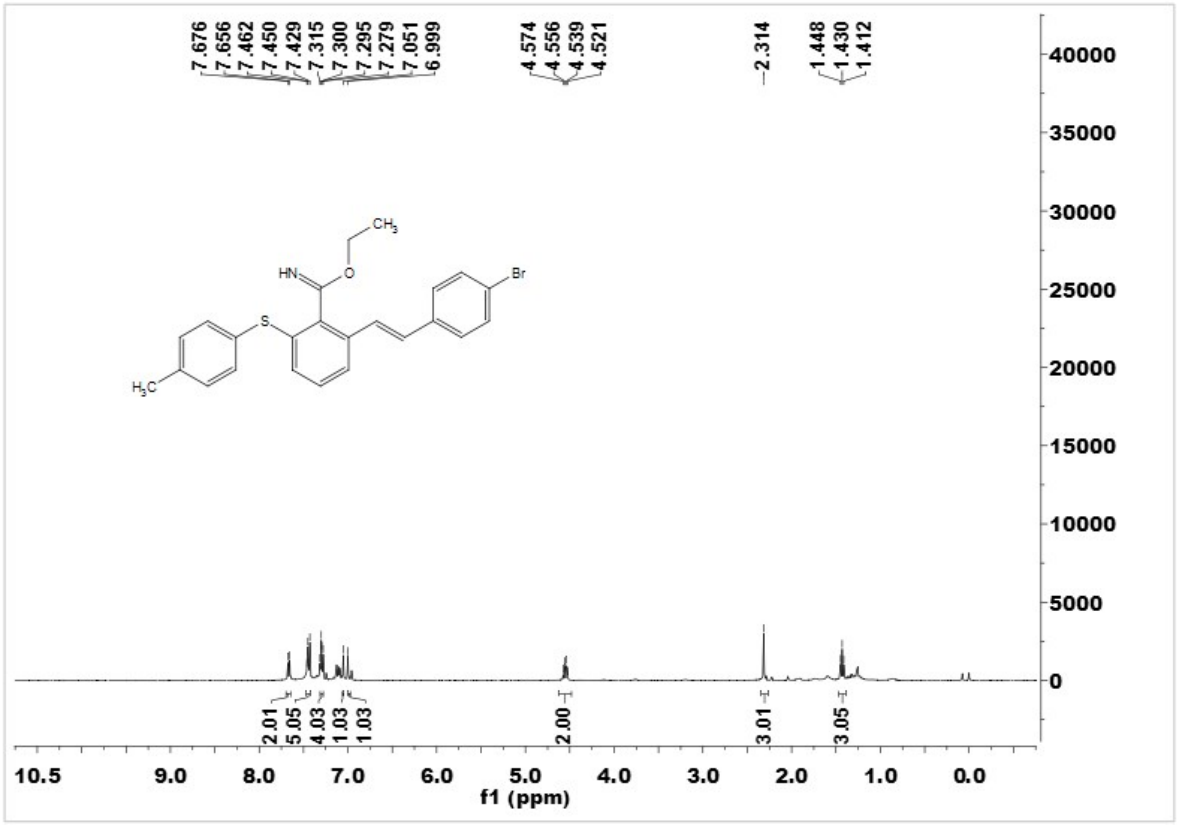


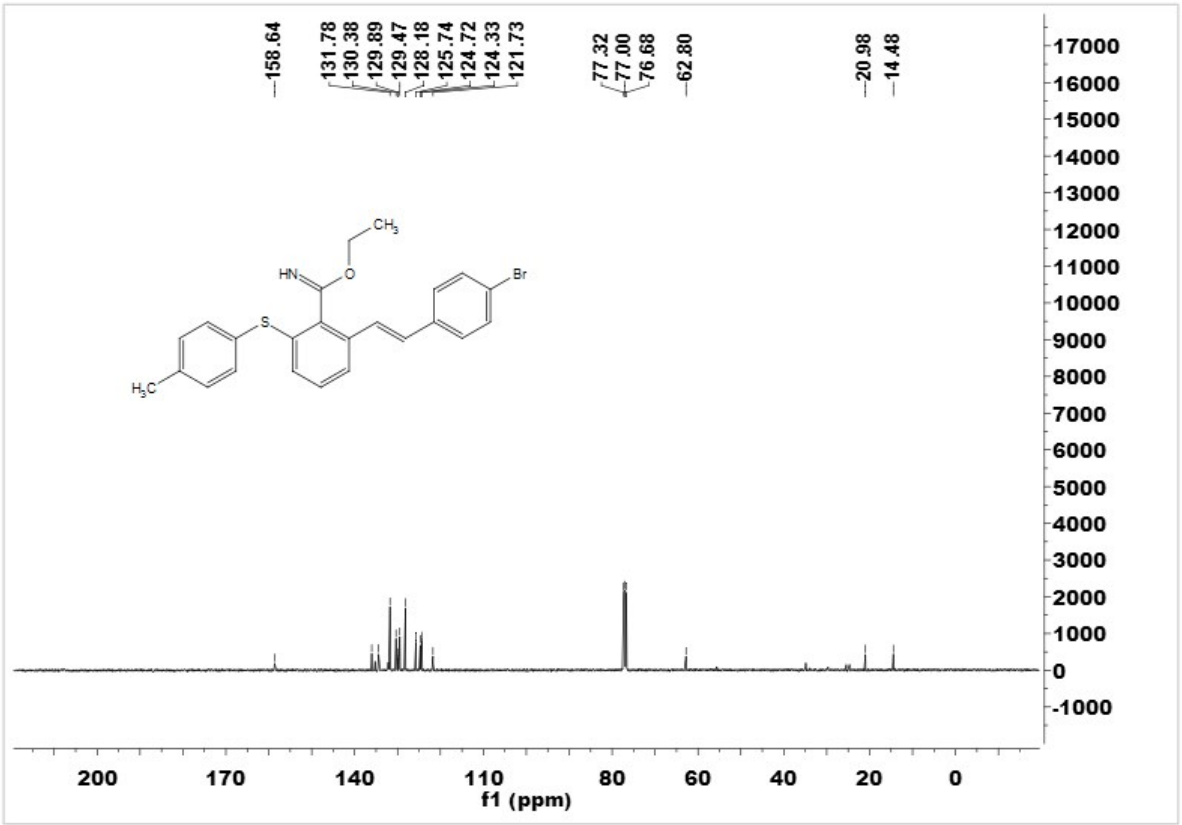
Ethyl (*E*)-2-(4-chlorostyryl)-6-(phenylthio)benzimidate (14d)



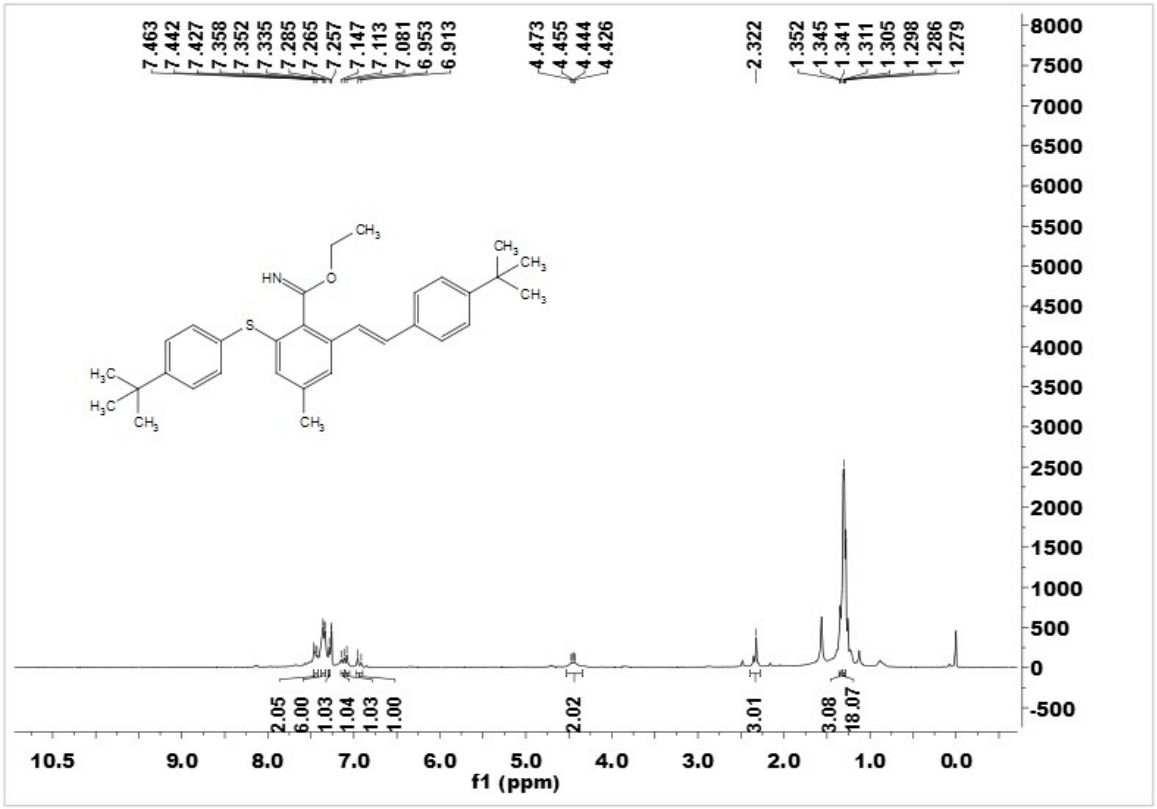


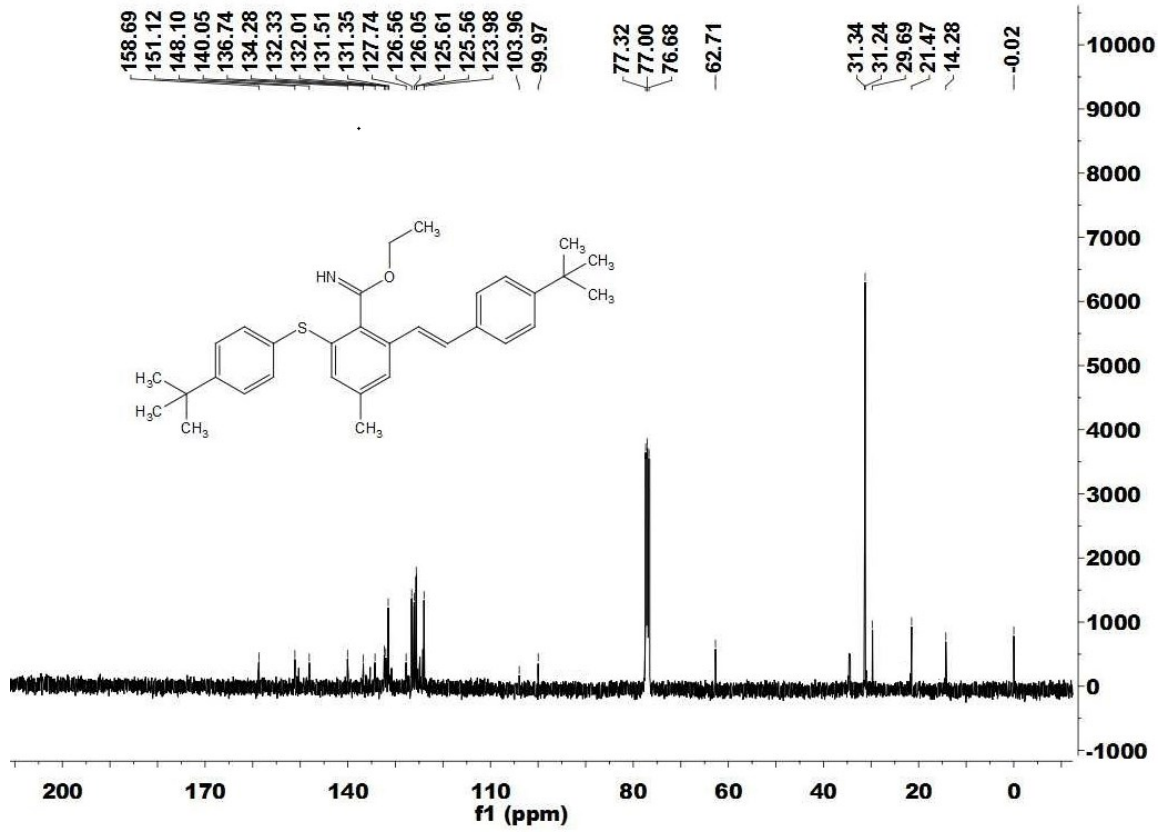
Ethyl (*E*)-2-(4-bromostyryl)-6-(*p*-tolylthio)benzimidate (14e)



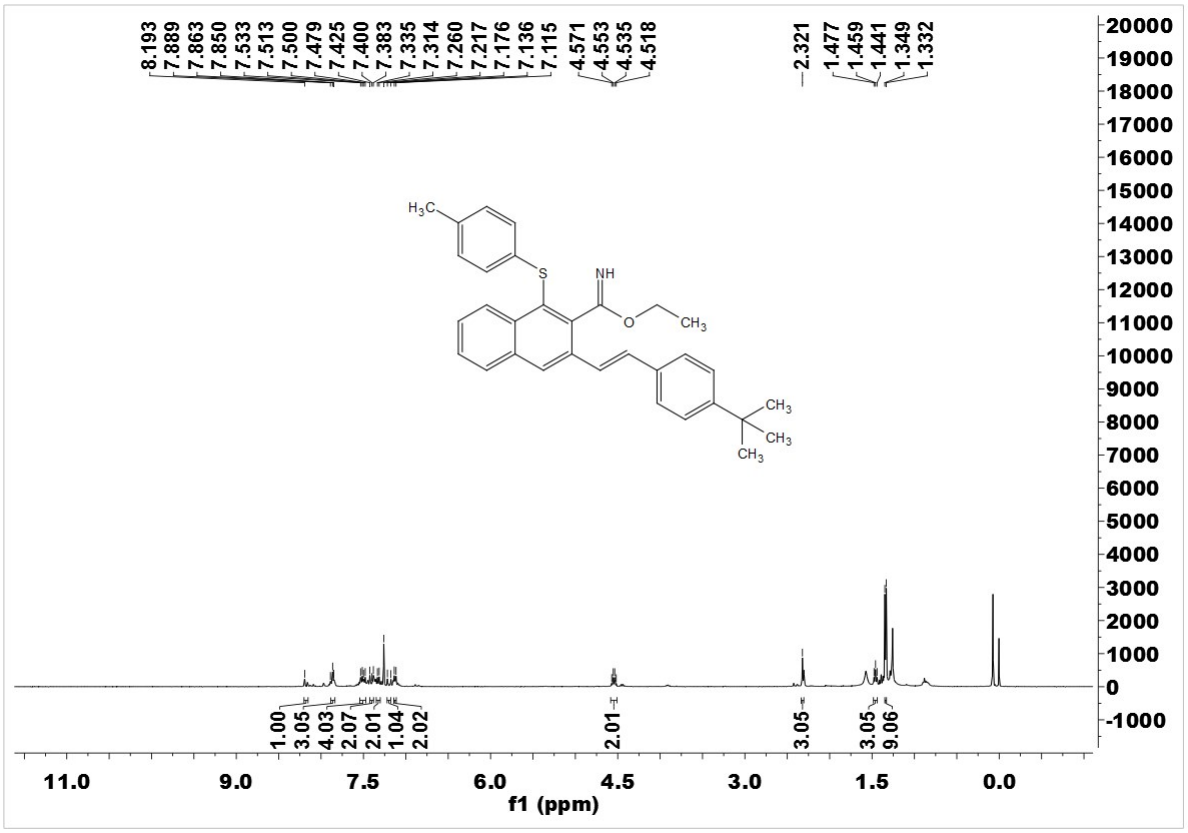


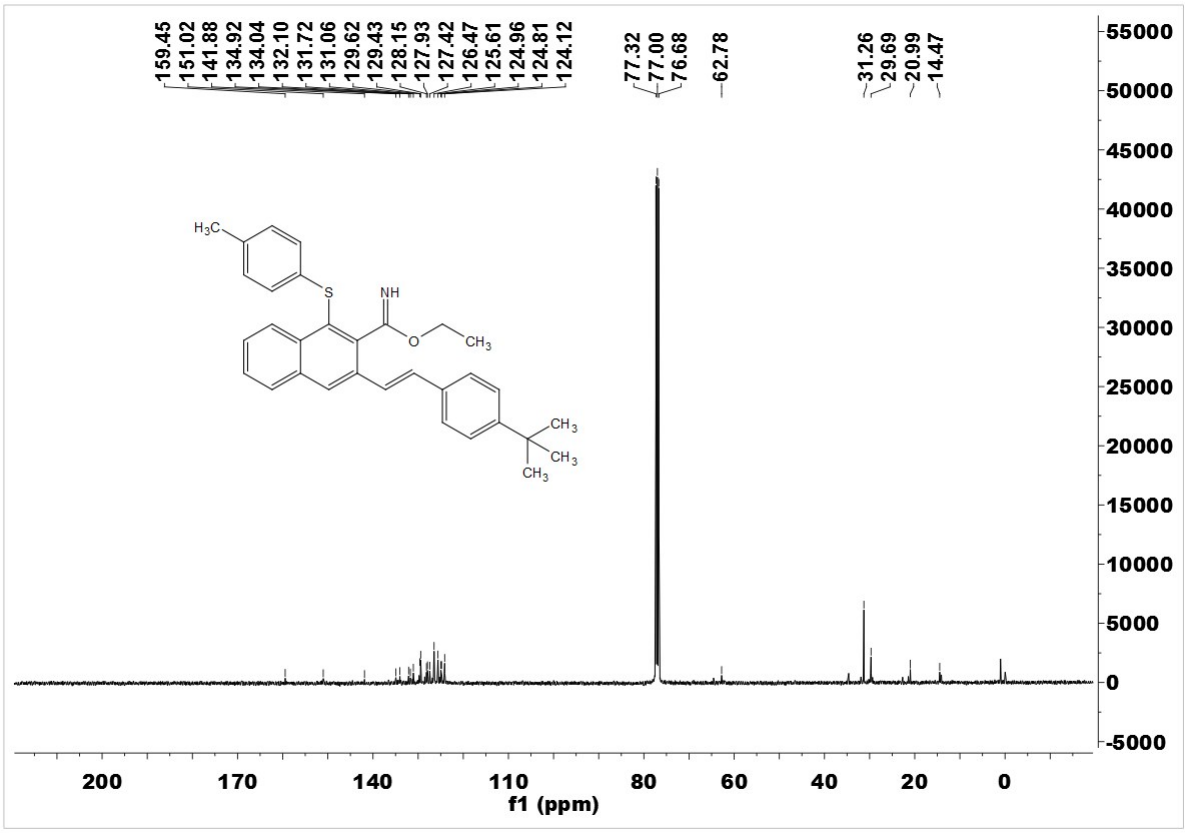
Ethyl (*E*)-2-((4-(*tert*-butyl)phenyl)thio)-6-(4-(*tert*-butyl)styryl)-4-methylbenzimidate (14f)



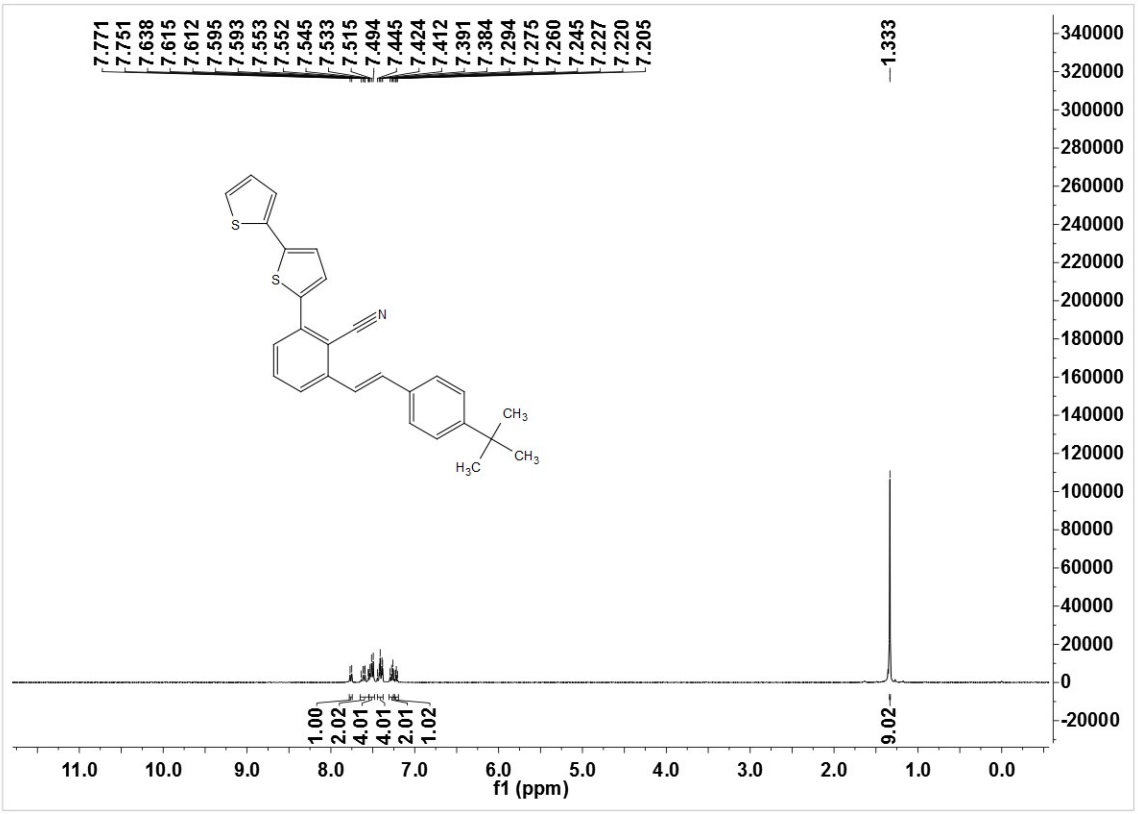


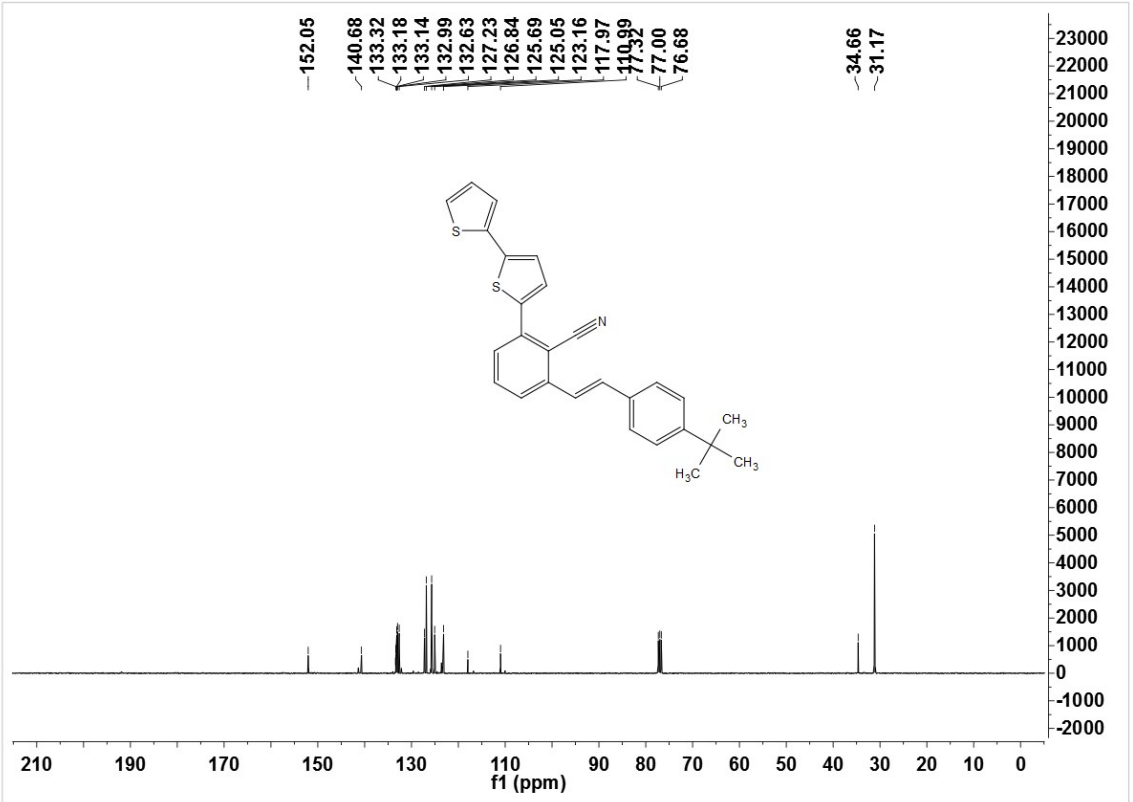
Ethyl (*E*)-3-(4-(*tert*-butyl)styryl)-1-(*p*-tolylthio)-2-naphthimidate (14g)





(*E*)-2-([2,2'-Bithiophen]-5-yl)-6-(4-(*tert*-butyl)styryl)benzonitrile (15a)





(*E*)-2-(Benzo[*b*]thiophen-2-yl)-6-(4-(*tert*-butyl)styryl)benzonitrile (15b)