SYNTHESIS Journal of Synthetic Organic Chemistry SUPPORTING INFORMATION

Supporting Information
for DOI: 10.1055/s-0032-1316821

Thieme

An Efficient Synthesis of 2-Aminothiophenes via the Gewald Reaction Catalyzed by an *N*-methylpiperazine Functionalized Polyacrylonitrile Fiber

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General experimental information

Reagents

Commercially available polyacrylonitrile fiber (PANF) with a length of 10 cm and diameter of 30±0.5 μm (from the Fushun Petrochemical Corporation of China) was used. Water was deionized. All reagents were analytical grade. Acetonitrile was dried by CaH_2. Toluene was refluxed by sodium before use. Ethyl cyanoacetate, malononitrile, 2,5-dihydroxy-1,4-dithiane, *N*-methylpiperazine and the other reagents were used without further purification. Column chromatography was performed on silica gel 200-300 mesh, and the eluent was a mixture of petroleum ether (PE, bp 60-90 °C) and ethyl acetate (EA).

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Acid exchange capacity of the fiber catalyst:

The acid exchange capacity was calculated according to the amount of acid consumed by P-PANF. Dried P-PANF (0.250 g) was immersed in 20.00 mL of HCl solution (0.100 M) for 6 h. Then the treated fiber was filtered out and washed with water. The concentration of the remaining HCl solution was titrated by 0.100 M NaOH.

Entry	Weight of P-PANF g	The consumed NaOH mL	Average mL	Acid exchange capacity mmol g^{-1}
1	0.250	14.25		
2	0.250	14.20	14.21	2.32
3	0.250	14.20		

The amount of acid consumed by P-PANF = 20.00 mL × 0.100 M – 14.21 mL × 0.100 M = 0.579 mmol

The acid exchange capacity of P-PANF = 0.579 mmol ÷ 0.250 g = 2.32 mmol g^{-1}

The determined acid exchange capacity of P-PANF was 2.32 mmol g^{-1}, indicating that 1.000 g P-PANF contains 1.16 mmol 3-(*N*-methylpiperazinyl)propyl groups (each group has two basic N atoms).

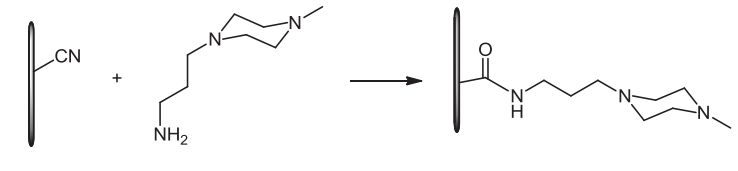
Unmodified PANF is composed by three parts: acrylonitrile (93.0%), methyl acrylate (6.5%) and sodium styrene sulfonate (0.5%).

Each CN group in PANF reacted with an *N*-methyl-*N*'-(3-aminopropyl)piperazine molecule and gets a ΔMW of 158.24 during the amination process. Each ester group reacted with an amine molecule and gets a ΔMW of 125.21. If each CN group have the same reaction opportunity as the ester group, we can give an average ΔMW = [158.24 × 0.930 + 125.21 × 0.065] ÷ (0.930+0.065) = 156.08.

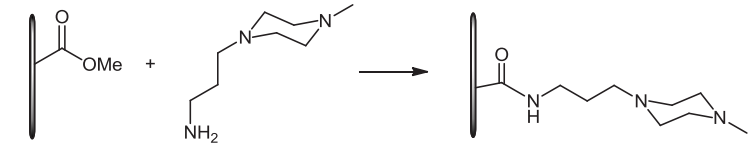
2.32 ÷ 2 ×156.08 = 0.181 g

0.181/ (1.000 – 0.181) = 22.1 %

The calculated weight gain of 22.1% is in accord with the measured weight gain of 23.0%.



MW: 26.02 MW: 157.26 MW: 184.26



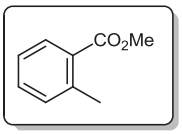
MW: 59.04 MW: 157.26 MW: 184.26

Synthesis of the activated nitriles

General procedure for synthesis of methyl carboxylate

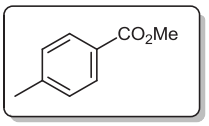
A carboxylic acid (150 mmol) was dissolved in 150 mL of methanol. Then 7.5 mL of concentrated sulfuric acid was added and the mixture was heated at reflux for 5 h. After cooling to room temperature the reaction mixture was evaporated under vacuum. Then 100 mL of water was added and the residue was neutralized with $NaHCO_3$. The mixture was extracted by 200 mL of CH_2C1_2. The organic layer was washed with H_2O, 5% aqueous $NaHCO_3$, and saturated NaCl solution and dried over Na_2SO_4. Evaporate the solvent to afford the desired product.[1,2]

(a) **Methyl 2-methylbenzoate**



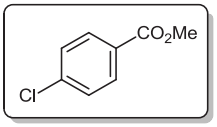
Yield: 15.8 g, 70%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 7.4 Hz, 1H), 7.44 – 7.38 (m, 1H), 7.30 – 7.22 (m, 2H), 3.91 (s, 3H), 2.63 (s, 3H).[3a]

(b) **Methyl 4-methylbenzoate**



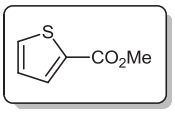
Yield: 21.2 g, 94%; white crystals; mp 30-32 °C (Lit.[3b] mp 35-36 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 3.90 (s, 3H), 2.40 (s, 3H).[3b]

(c) **Methyl 4-chlorobenzoate**



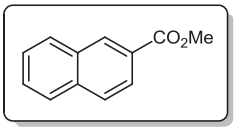
Yield: 24.6 g, 96%; white crystals; mp 42-44 °C (Lit.[2] mp 42-44 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 3.91 (s, 3H).[2]

(d) **Methyl 2-thiophenecarboxylate**



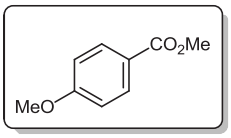
Yield: 19.2 g, 90%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 – 7.77 (m, 1H), 7.55 – 7.51 (m, 1H), 7.10 – 7.06 (m, 1H), 3.87 (s, 3H).[3c]

(e) **Methyl 2-naphthoate**



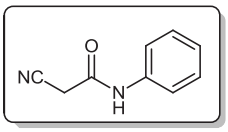
Yield: 27.4 g, 98%; white solid; mp 74-75 °C (Lit.[4a] mp 75-77 °C); ^{1}H NMR (400 MHz, DMSO): δ = 8.63 (s, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 8.05 – 7.97 (m, 3H), 7.70 – 7.58 (m, 2H), 3.92 (s, 3H).[4b]

Synthesis of methyl 4-methoxybenzoate[5]



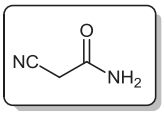
Methyl 4-hydroxybenzoate (15.2 g, 100 mmol) was dissolved in 200 mL of dry DMF. K_2CO_3 (49.8 g, 360 mmol) was added and the suspension was stirred for 30 min. Methyliodide (14.4 g, 100 mmol) was then added dropwise. After stirring for 20 h, 200 mL of water was added. The precipitate was then filtered and washed with 100 mL of cold water to afford the target product as a white solid (yield: 13.0 g, 78%). Mp 46-47 °C, (Lit.[5] mp 51-52 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H), 3.85 (s, 3H).[5]

Synthesis of 2-cyano-*N*-phenylacetamide[6]



Aniline (9.3 g, 100 mmol) was dissolved in 100 mL of DMF. Then ethyl cyanoacetate (11.3 g, 100 mmol) was added and the mixture was heated at reflux for 6 h. And then 150 mL of water was added slowly. The precipitate was filtered and washed with cold water, then recrystallized from ethanol to give the aimed product as a white solid (yield: 11.5 g, 72%). Mp. 195-196 °C (Lit.[6b] 193 °C). ^{1}H NMR (400 MHz, DMSO): δ = 10.28 (s, 1H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.37 – 7.29 (m, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 3.89 (s, 2H).[6c]

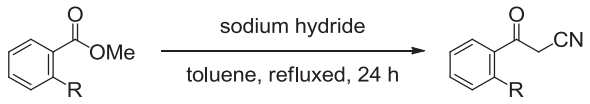
Synthesis of 2-cyanoacetamide[7]



Ethyl cyanoacetate (5.7 g, 50 mmol) was dropped into 49 mL of aqueous ammonia (25%). The mixture was stirred for 1 h; then warms up a little. The flask was allowed to stand 2 h in an ice-salt mixture. The precipitate was filtered and washed with cold ethanol, then recrystallized from 95% ethanol to give the 2-cyanoacetamide as a white solid (yield: 1.6 g, 38%). Mp 113 °C (Lit.[7a] mp 119-120 °C). ^{1}H NMR (400 MHz, DMSO): δ = 7.63 (s, 1H), 7.32 (s, 1H), 3.57 (s, 2H).[7b]

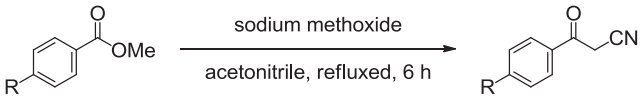
General procedure for synthesis of benzoylacetonitriles and other activated nitriles

Method A. An ester (100 mmol) and acetonitrile (12.5 mL, 300 mmol) were dissolved in 100 mL of toluene, then sodium hydride (80%, 9.0 g, 300 mmol) was added and the reaction mixture was heated to reflux for 24 h. After cooling to room temperature, it was filtered and washed with 30 mL of CH_2Cl_2. The solid material was dissolved in 100 mL of water and cooling ice/salt mixture. Then HCl 15% was added until pH = 2-3 and in a manner that its temperature shall not exceed 5 °C. The precipitate was filtered and washed with water until neutral, then recrystallized from ethanol to give the desired product.[8]



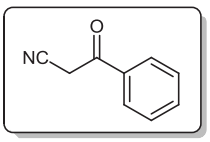
R = H or Me

Method B. An ester (100 mmol) was dissolved in 200 mL of dry acetonitrile. Sodium methoxide (10.8 g, 200 mmol) was added and the reaction mixture was heated at reflux under the protection of nitrogen for 6 h. After cooling to room temperature, 200 mL of H_2O was added and the reaction mixture was washed with CH_2Cl_2 (3×150 mL). The aqueous layer was adjusted to pH = 7 using 10% aq citric acid and the product precipitated upon standing. The precipitate was filtered and then recrystallized from ethanol to give the target product.[2]



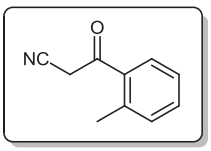
R = Me, OMe, Cl

(a) **Benzoylacetonitrile** (Method A)



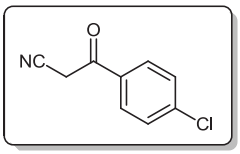
Yield: 9.6 g, 66%; light yellow crystals; mp 75-76 °C (Lit.[8b] mp 81 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 7.6 Hz, 2H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.56 – 7.49 (m, 2H), 4.14 (s, 2H).[9]

(b) **2-Methylbenzoylacetonitrile** (Method A)



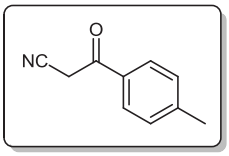
Yield: 10.7 g, 67%; light yellow crystals; mp 78-79 °C (Lit.[9] mp 86-88 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 7.6 Hz, 1H), 7.51 – 7.45 (m, 1H), 7.36 – 7.29 (m, 2H), 4.07 (s, 2H), 2.57 (s, 3H).[9]

(c) **4-Chlorobenzoylacetonitrile** (Method B)



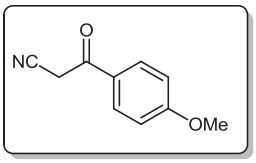
Yield: 12.6 g, 70%; light yellow crystals; mp 125-126 °C (Lit.[2] mp 126-128 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.6 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H), 4.09 (s, 2H).[2]

(d) **4-Methylbenzoylacetonitrile** (Method B)



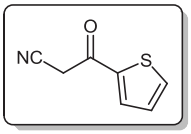
Yield: 9.7 g, 61%; white crystals; mp 100-101 °C (Lit.[8c] mp 94-96 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 4.06 (s, 2H), 2.44 (s, 3H).[9]

(e) **4-Methoxybenzoylacetonitrile** (Method B)



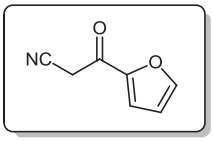
Yield: 8.8 g, 50%; white crystals; mp 128-129 °C (Lit.[9] mp 123-126 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 8.9 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 4.03 (s, 2H), 3.90 (s, 3H).[9]

(f) **2-Thiophenoylacetonitrile** (Method A)



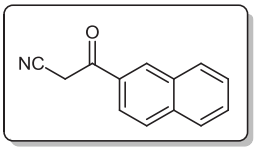
Yield: 8.5 g, 56%; light yellow crystals; mp 123-126 ^{o}C; (Lit.[10] mp 124-126 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 – 7.70 (m, 2H), 7.19 – 7.11 (m, 1H), 4.02 (s, 2H).[10]

(g) **2-Furoylacetonitrile** (Method A)



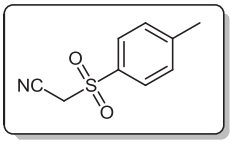
Yield: 8.1 g, 60%; light yellow crystals; mp 66-68 °C (Lit.[10] mp 66-68 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (s, 1H), 7.39 (d, *J* = 3.3 Hz, 1H), 6.65 (dd, *J* = 1.7, 1.6 Hz, 1H), 3.98 (s, 2H).[10]

(h) **2-Naphthoylacetonitrile** (Method A)



Yield: 9.8 g, 50%; yellow crystals; mp 122-123 °C (Lit.[11] mp 124 °C). ^{1}H NMR (400 MHz, DMSO): δ = 8.66 (s, 1H), 8.15 – 7.93 (m, 4H), 7.74 – 7.63 (m, 2H), 4.91 (s, 2H).[11]

Synthesis of tosylacetonitrile[12]



A mixture of sodium 4-methylbenzenesulfinate (8.9 g, 50 mmol) and 2-chloroacetonitrile (5.7 g, 75 mmol) was stirred at 60 °C for 2 h in 20 mL of PEG-400. The reaction mixture was poured into 300 mL of water. The precipitate was filtered and washed with cold ethanol, then recrystallized from ethanol to give the desired product as a light yellow solid (yield: 8.7 g, 89%). Mp: 144-146 °C (Lit.[12a] 147-148 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 4.05 (s, 2H), 2.50 (s, 3H).[12b]

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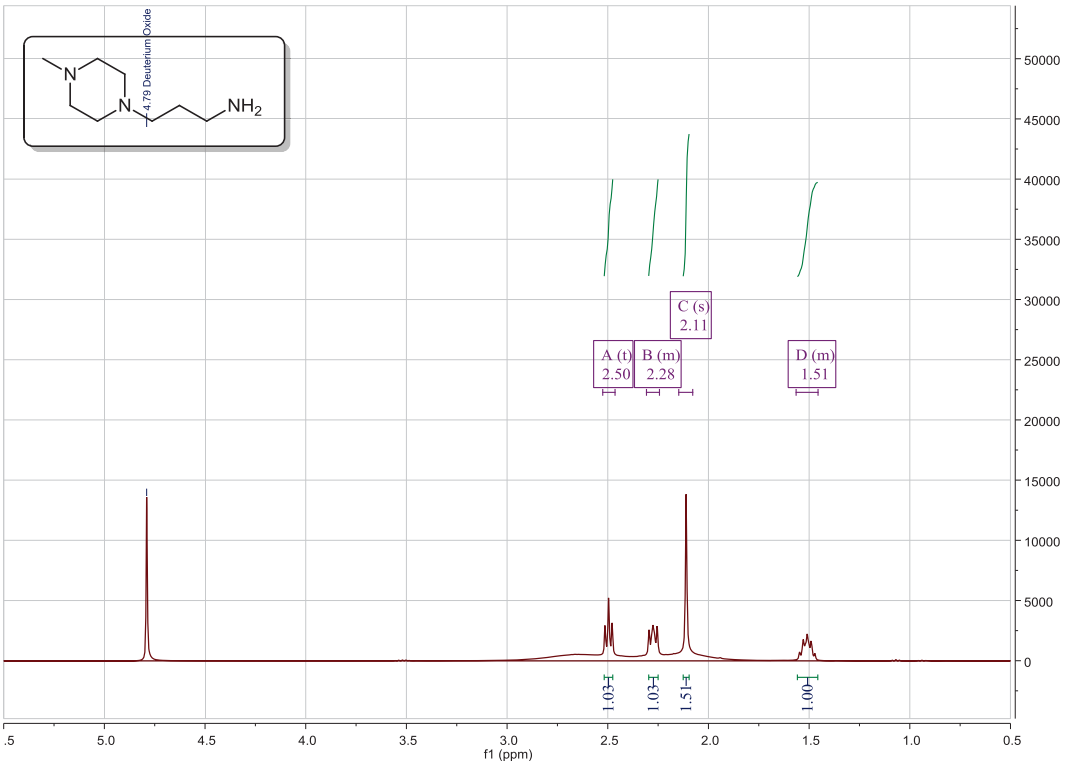
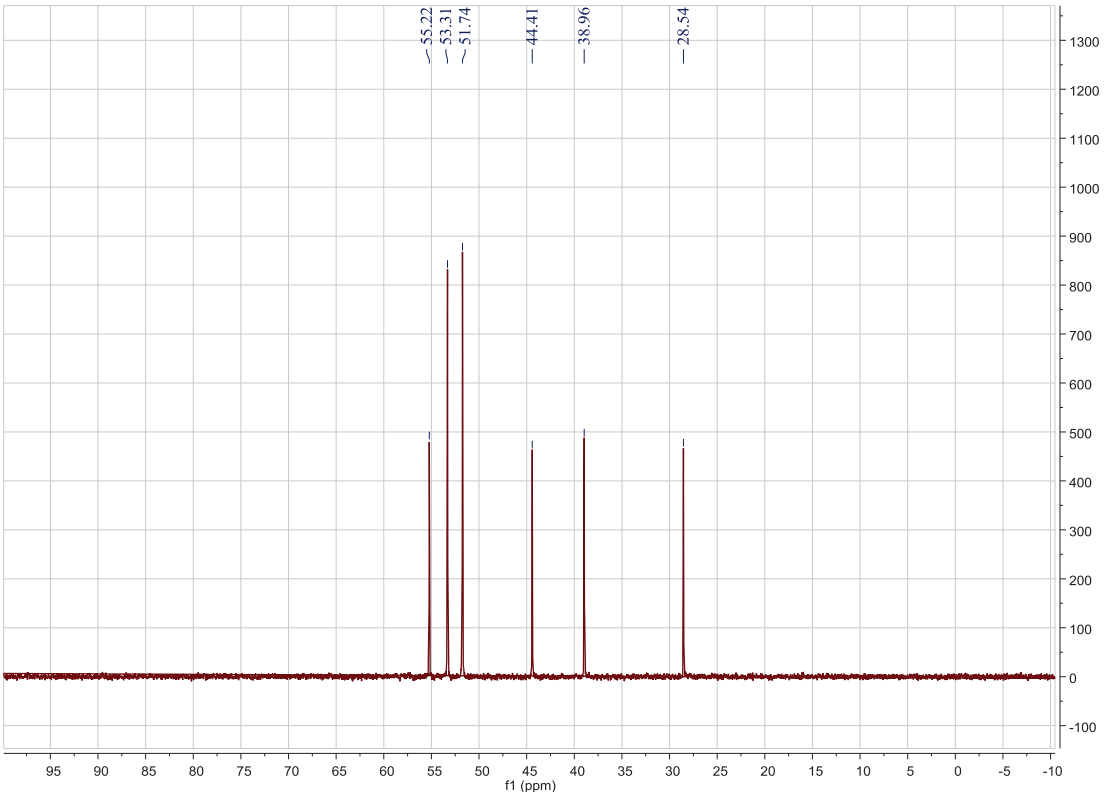
NMR Spectra

_N_-methyl-_N_'-(3-aminopropyl)piperazine

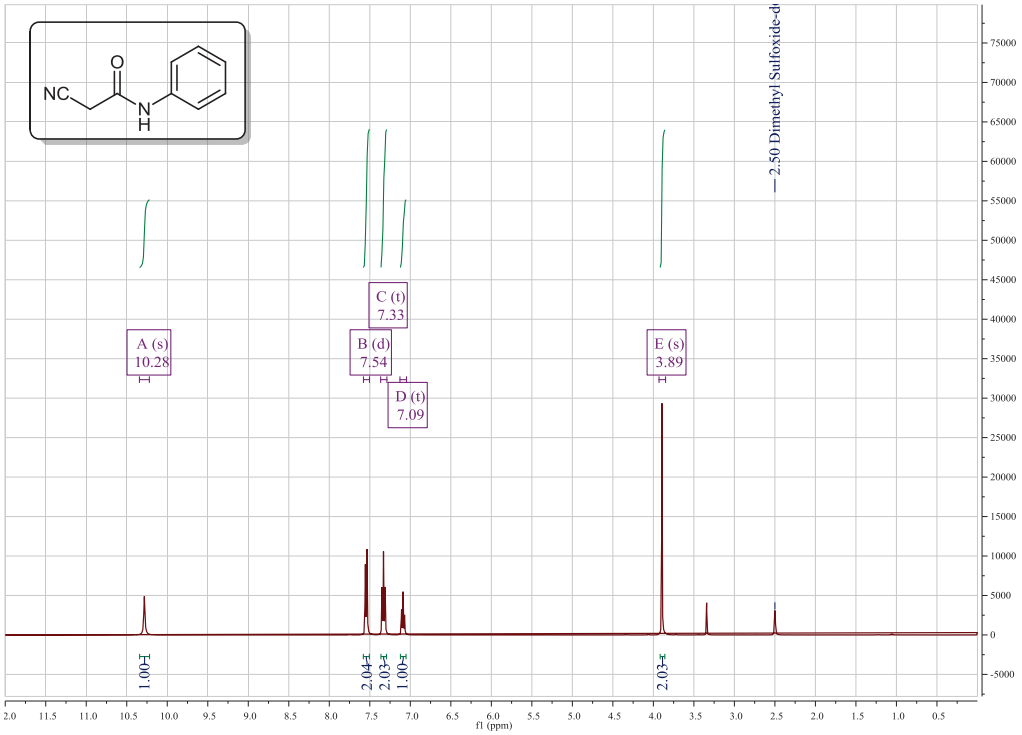


The ^{1}H NMR spectrum of *N*-methyl-*N*'-(3-aminopropyl)piperazine



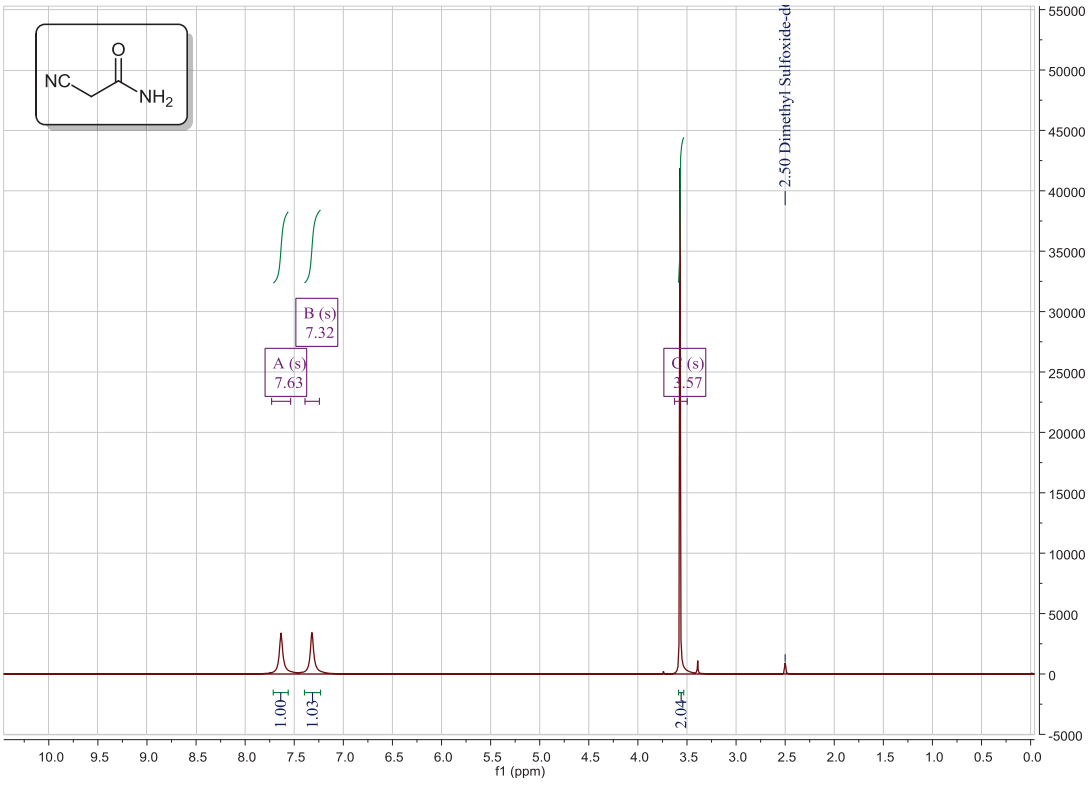
The ^{13}C NMR spectrum of *N*-methyl-*N*'-(3-aminopropyl)piperazine

2-Cyano-*N*-phenylacetamide



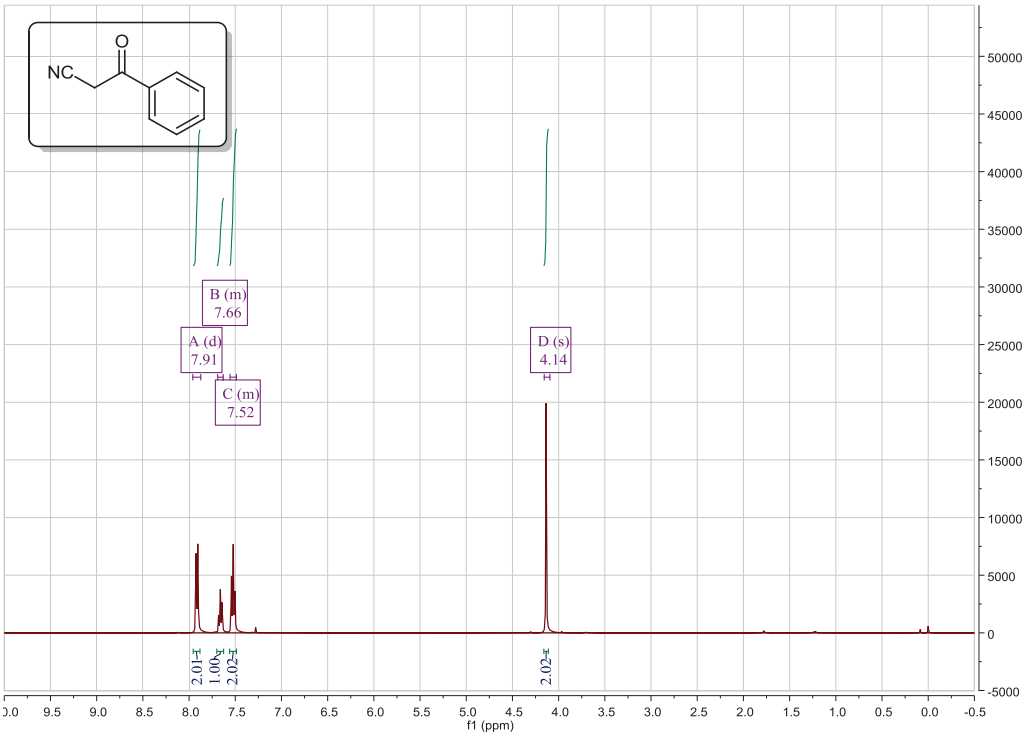
The ^{1}H NMR spectrum of 2-Cyano-*N*-phenylacetamide

2-Cyanoacetamide



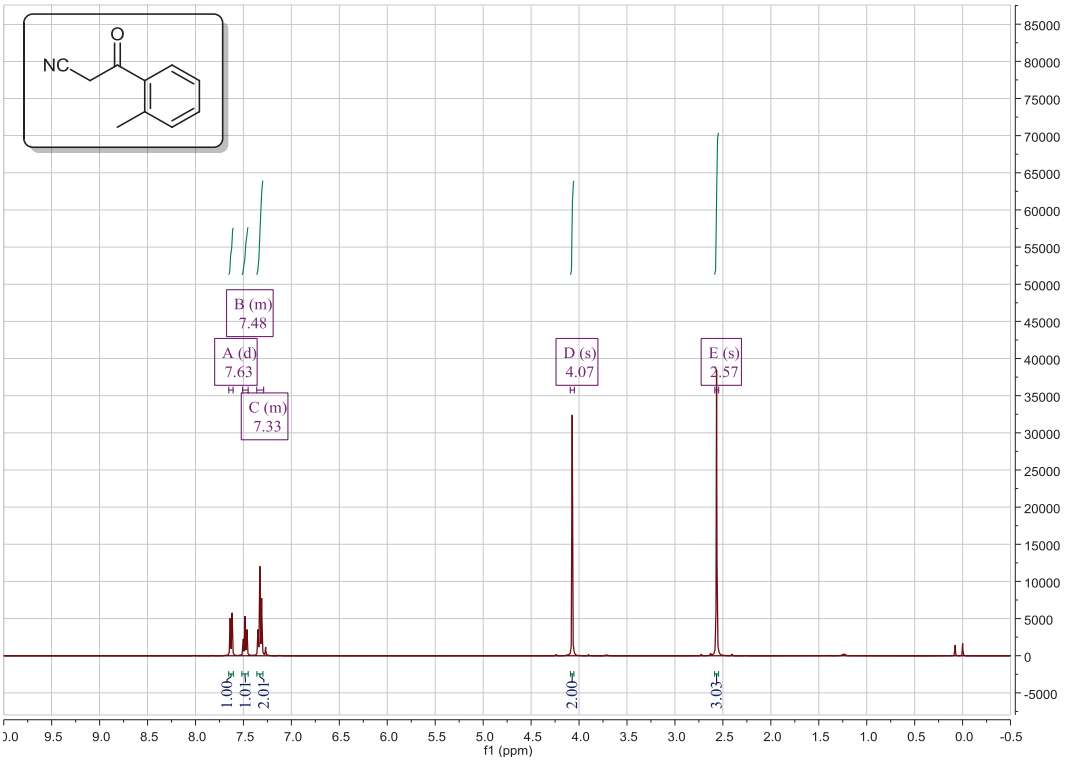
The ^{1}H NMR spectrum of 2-cyanoacetamide

Benzoylacetonitrile



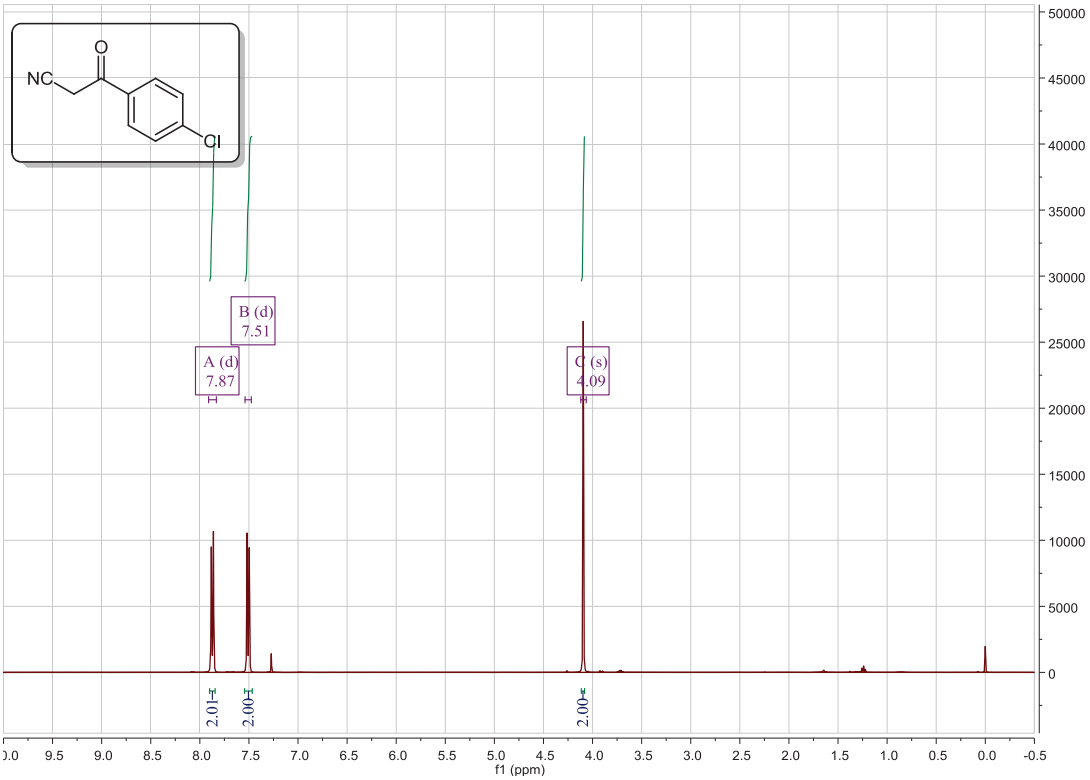
The ^{1}H NMR spectrum of benzoylacetonitrile

2-Methylbenzoylacetonitrile



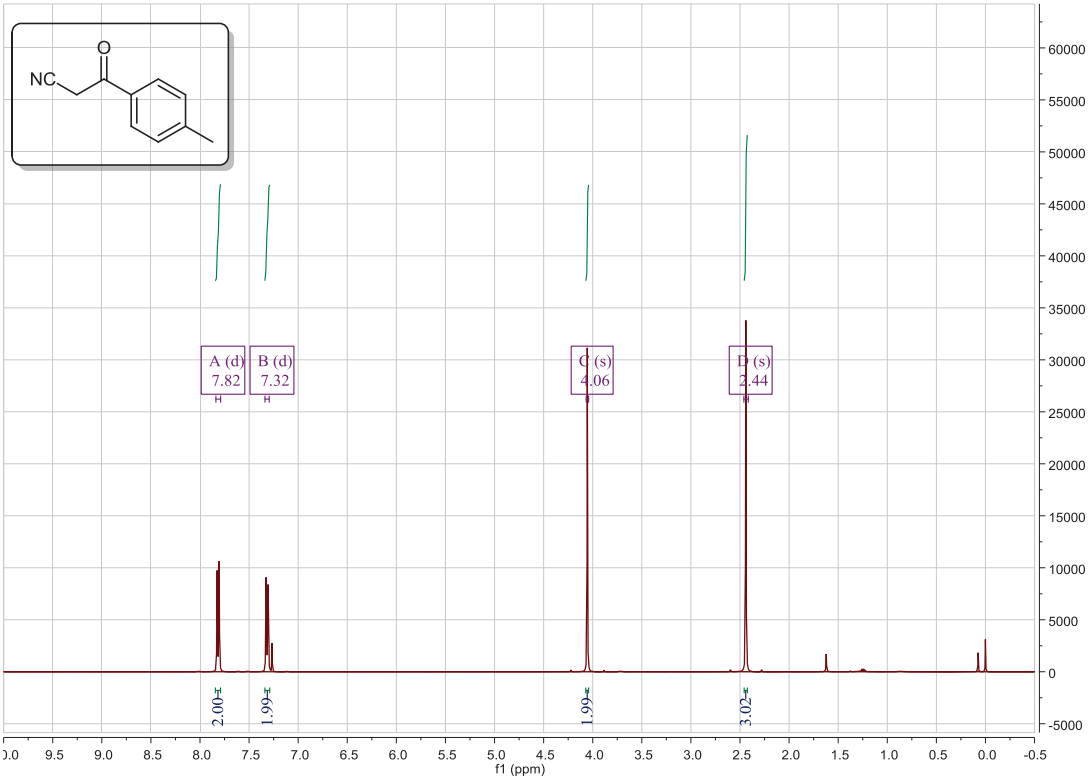
The ^{1}H NMR spectrum of 2-methylbenzoylacetonitrile

4-Chlorobenzoylacetonitrile



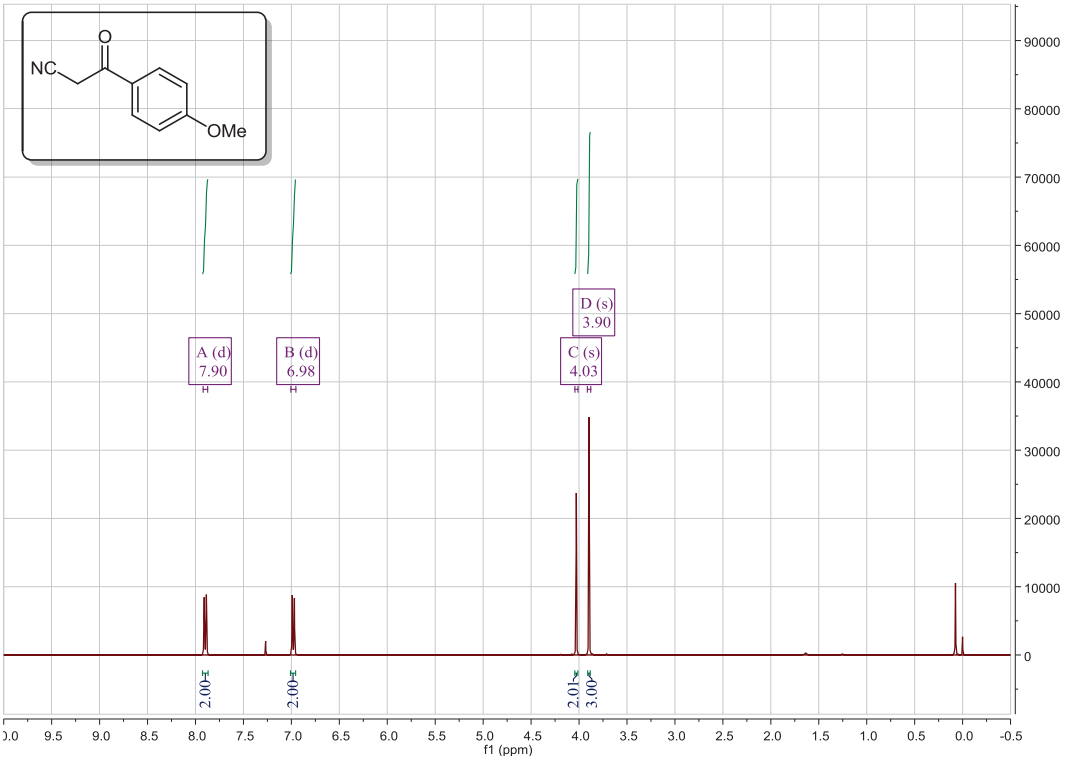
The ^{1}H NMR spectrum of 4-chlorobenzoylacetonitrile

4-Methylbenzoylacetonitrile



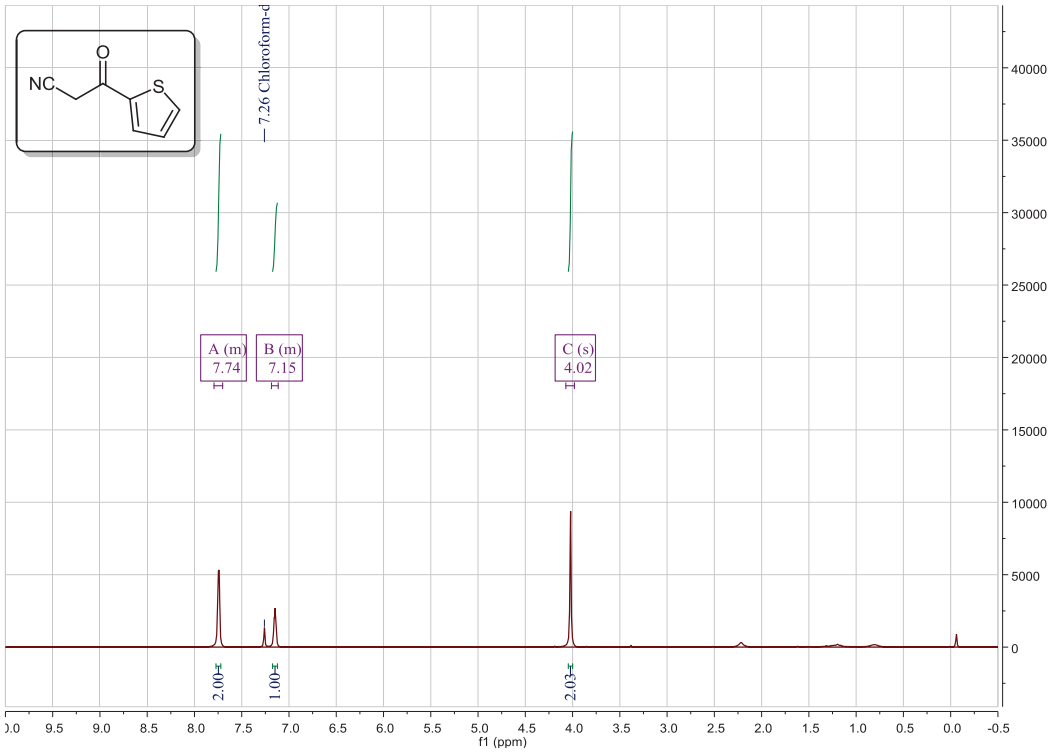
The ^{1}H NMR spectrum of 4-methylbenzoylacetonitrile

4-Methoxybenzoylacetonitrile



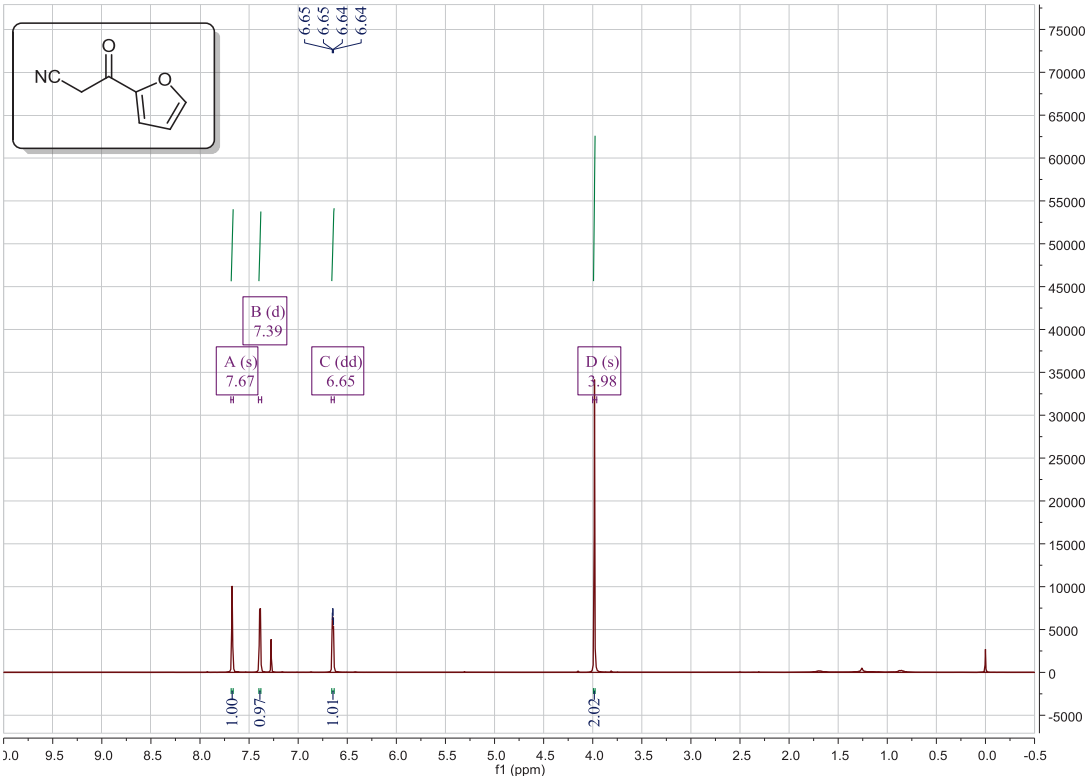
The ^{1}H NMR spectrum of 4-methoxybenzoylacetonitrile

2-Thiophenoylacetonitrile



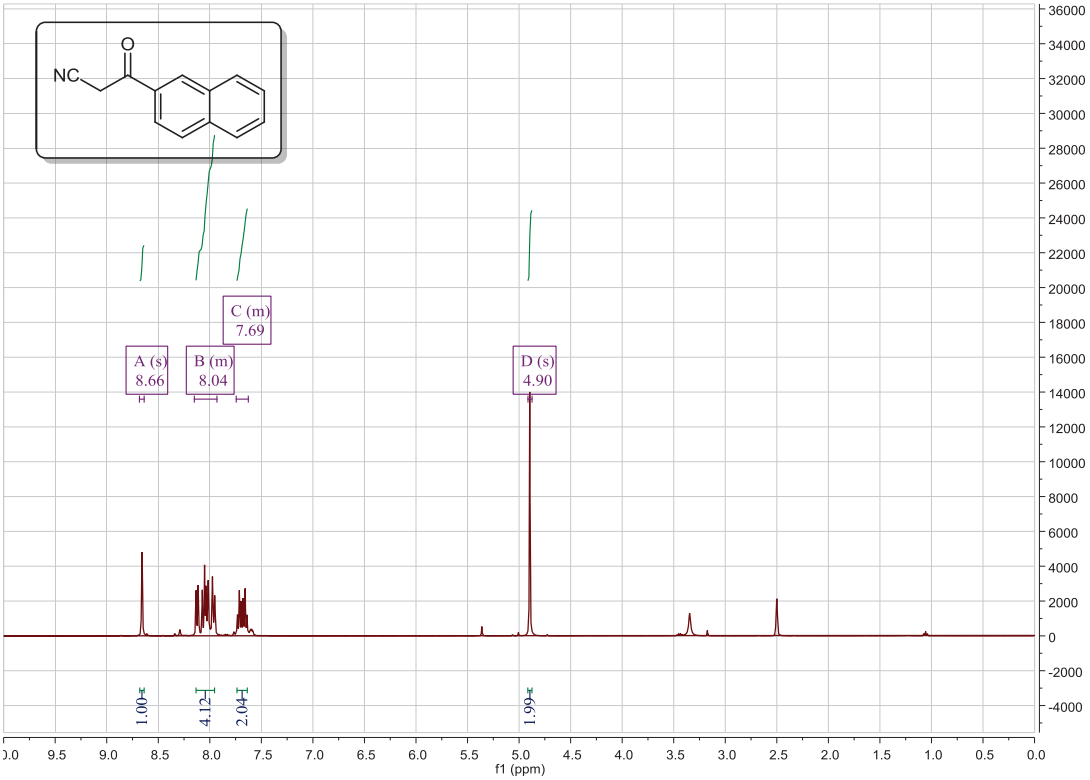
The ^{1}H NMR spectrum of 2-thiophenoylacetonitrile

2-Furoylacetonitrile



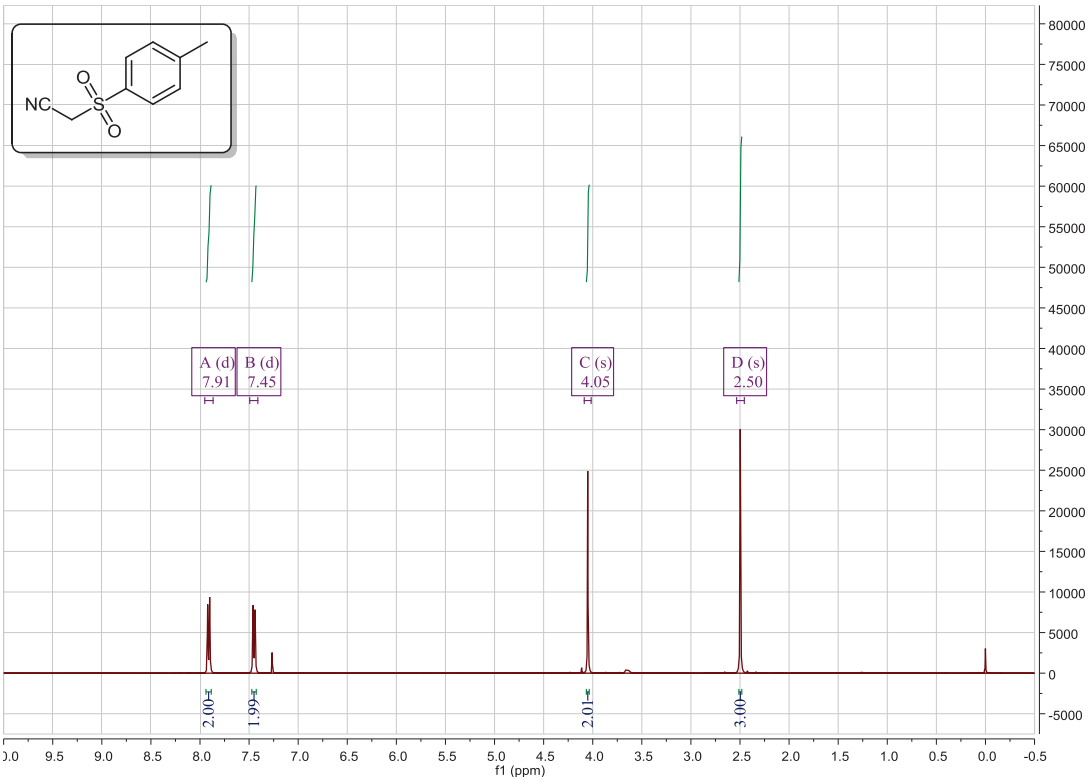
The ^{1}H NMR spectrum of 2-furoylacetonitrile

2-Naphthoylacetonitrile



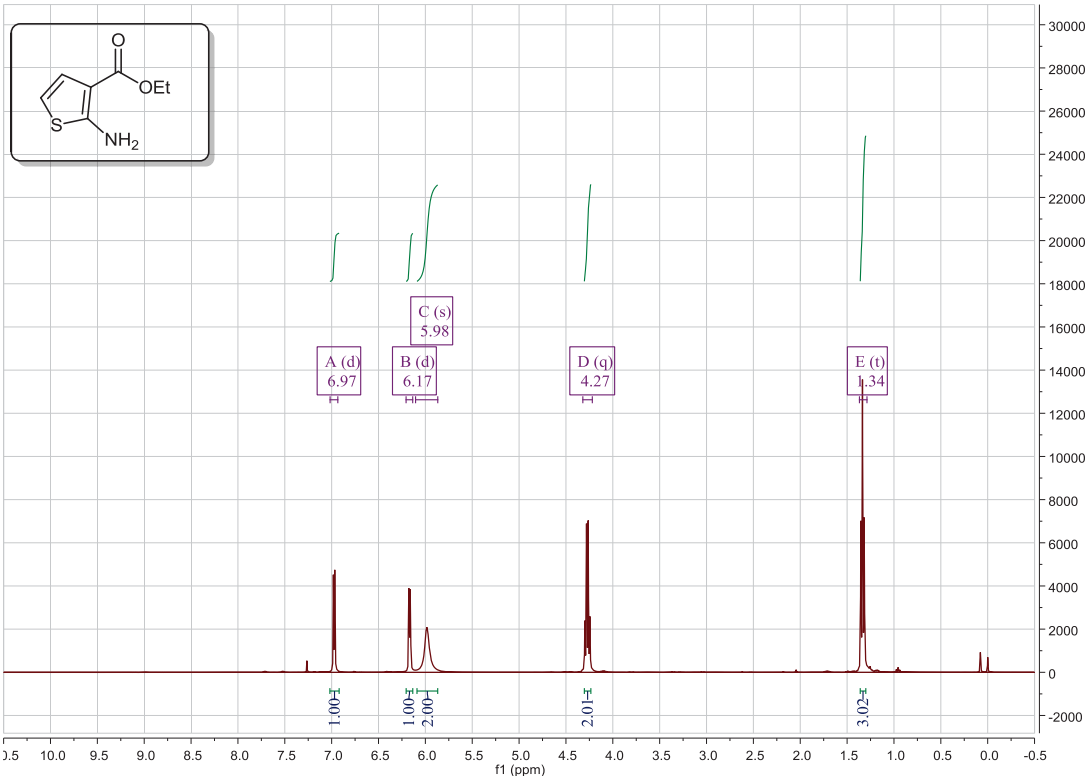
The ^{1}H NMR spectrum of 2-naphthoylacetonitrile

Tosylacetonitrile

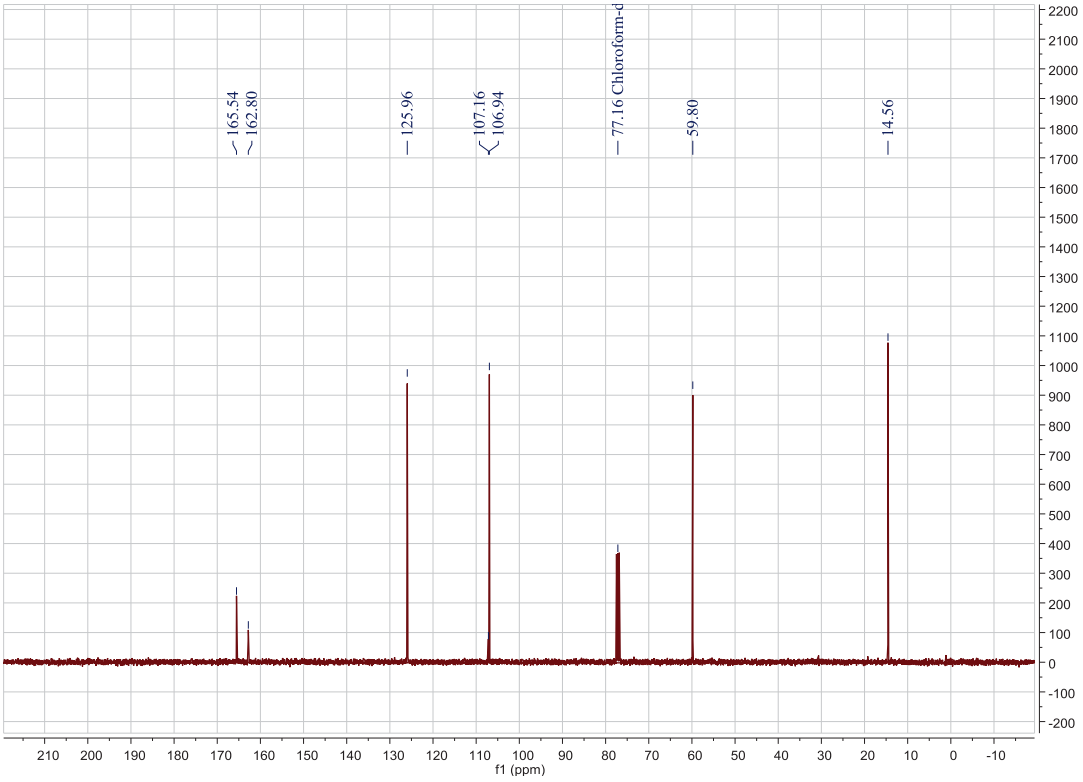


The ^{1}H NMR spectrum of tosylacetonitrile

Ethyl 2-aminothiophene-3-carboxylate (**5a**, Table 5, Entry 1)

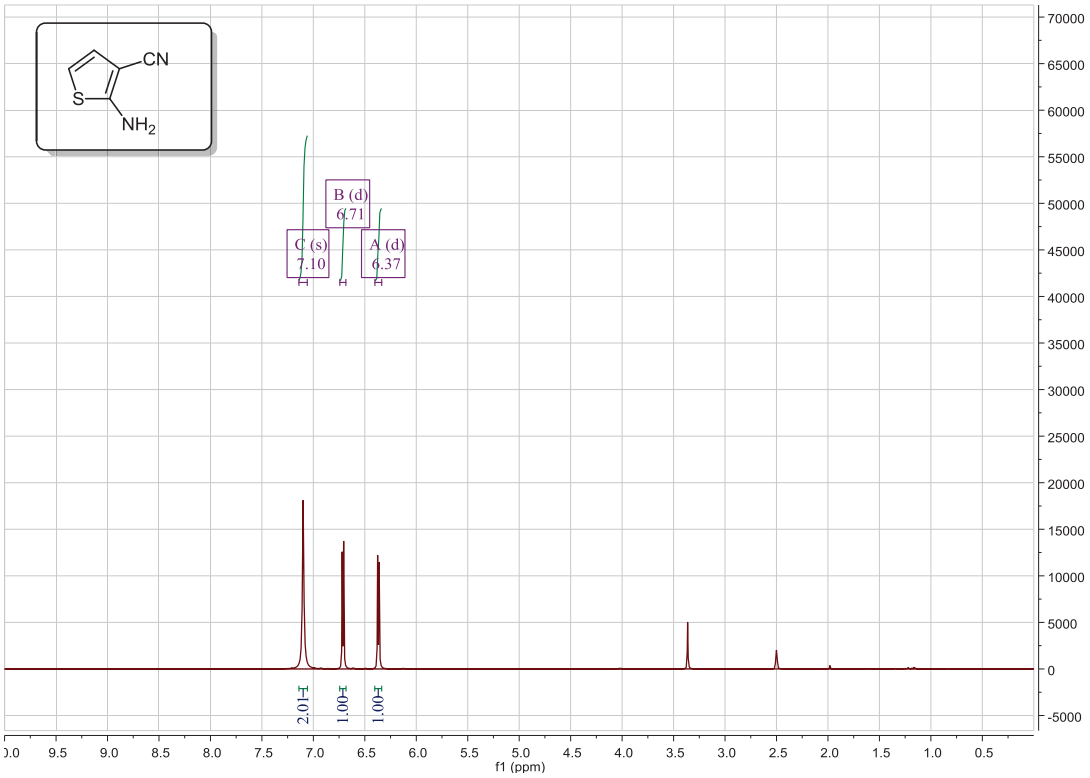


The ^{1}H NMR spectrum of ethyl 2-aminothiophene-3-carboxylate

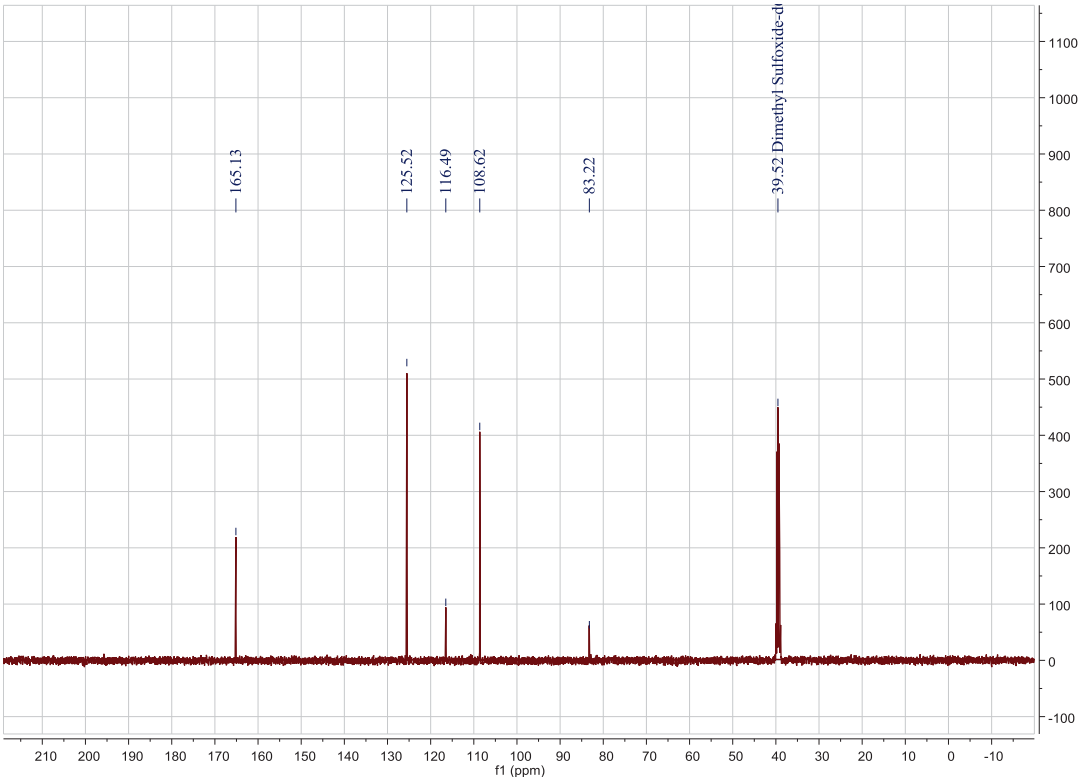


The ^{13}C NMR spectrum of ethyl 2-aminothiophene-3-carboxylate

2-Aminothiophene-3-carbonitrile (**5b**, Table 5, Entry 2)

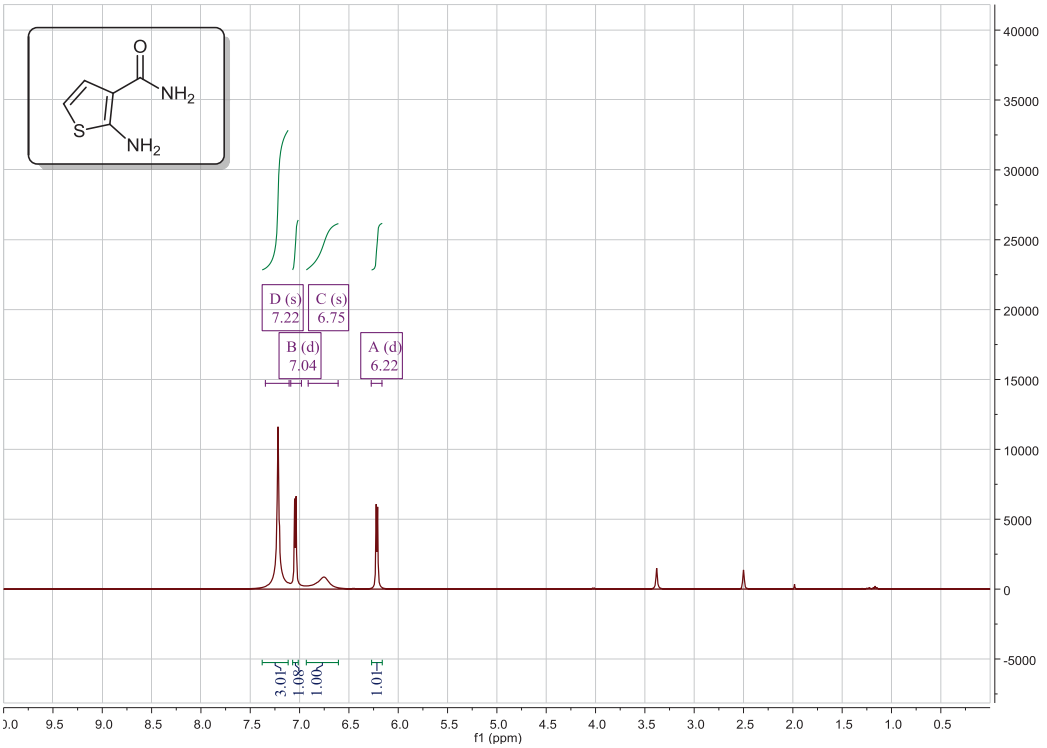


The ^{1}H NMR spectrum of 2-aminothiophene-3-carbonitrile

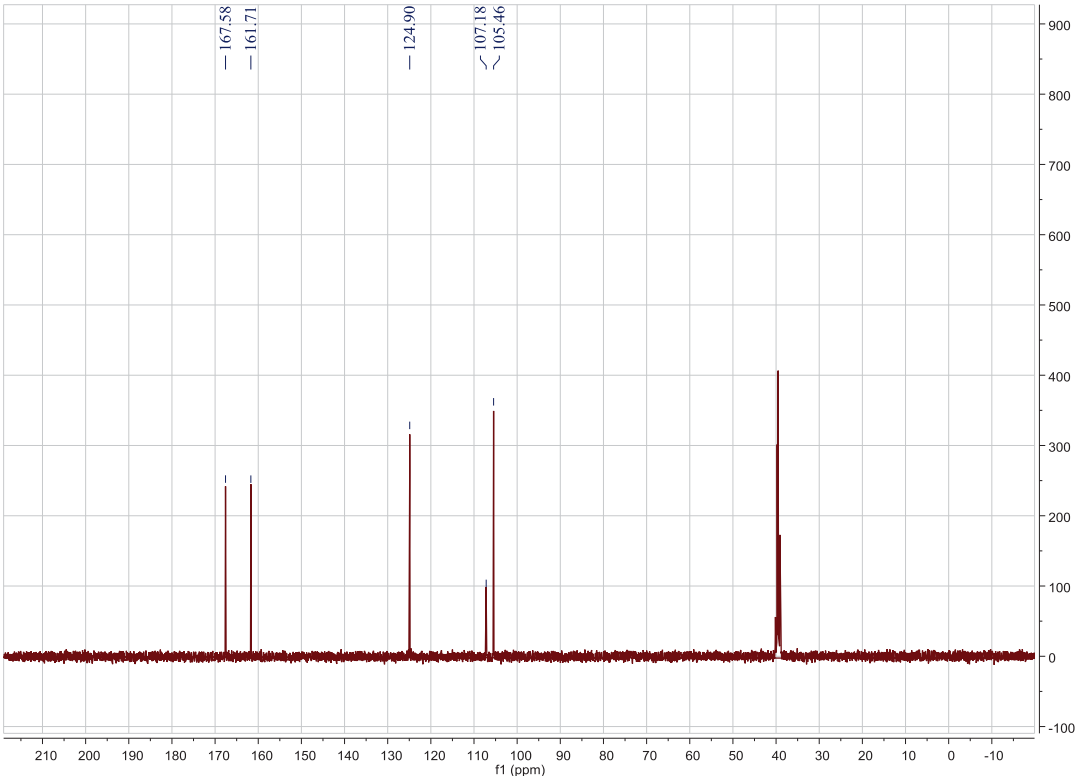


The ^{13}C NMR spectrum of 2-aminothiophene-3-carbonitrile

2-Aminothiophene-3-carboxamide (**5c**, Table 5, Entry 3)



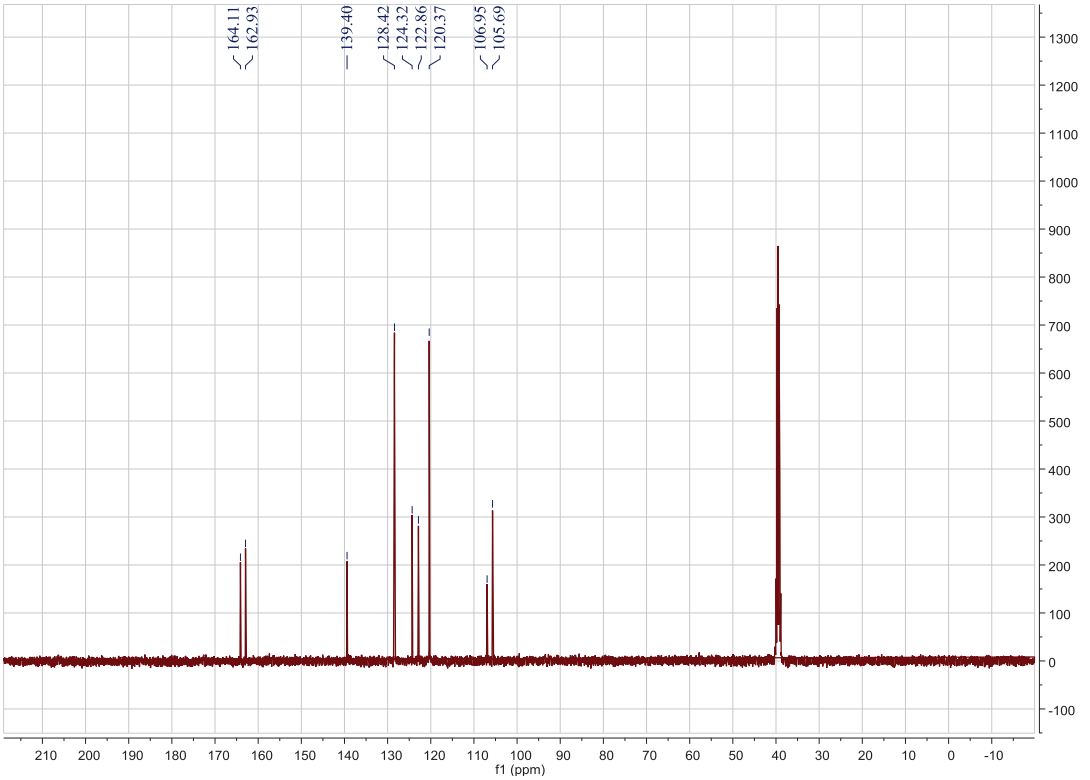
The ^{1}H NMR spectrum of 2-aminothiophene-3-carboxamide



The ^{13}C NMR spectrum of 2-aminothiophene-3-carboxamide

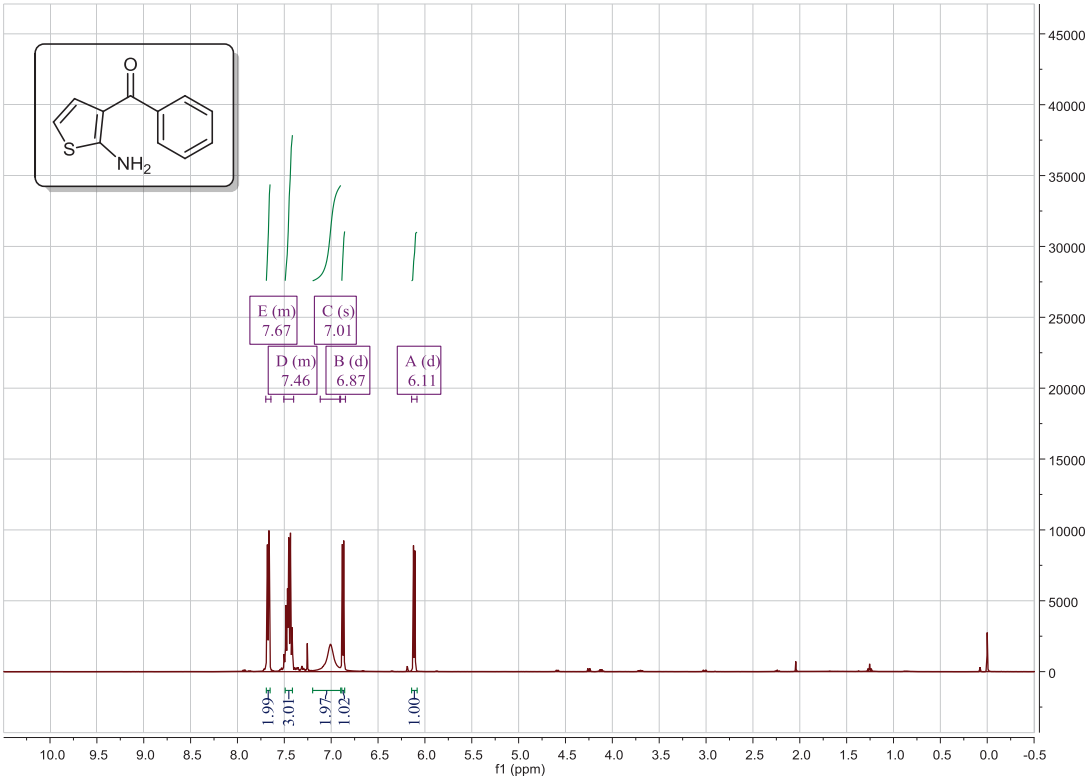
2-Amino-*N*-phenylthiophene-3-carboxamide (**5d**, Table 5, Entry 4)

The ^{1}H NMR spectrum of 2-amino-*N*-phenylthiophene-3-carboxamide

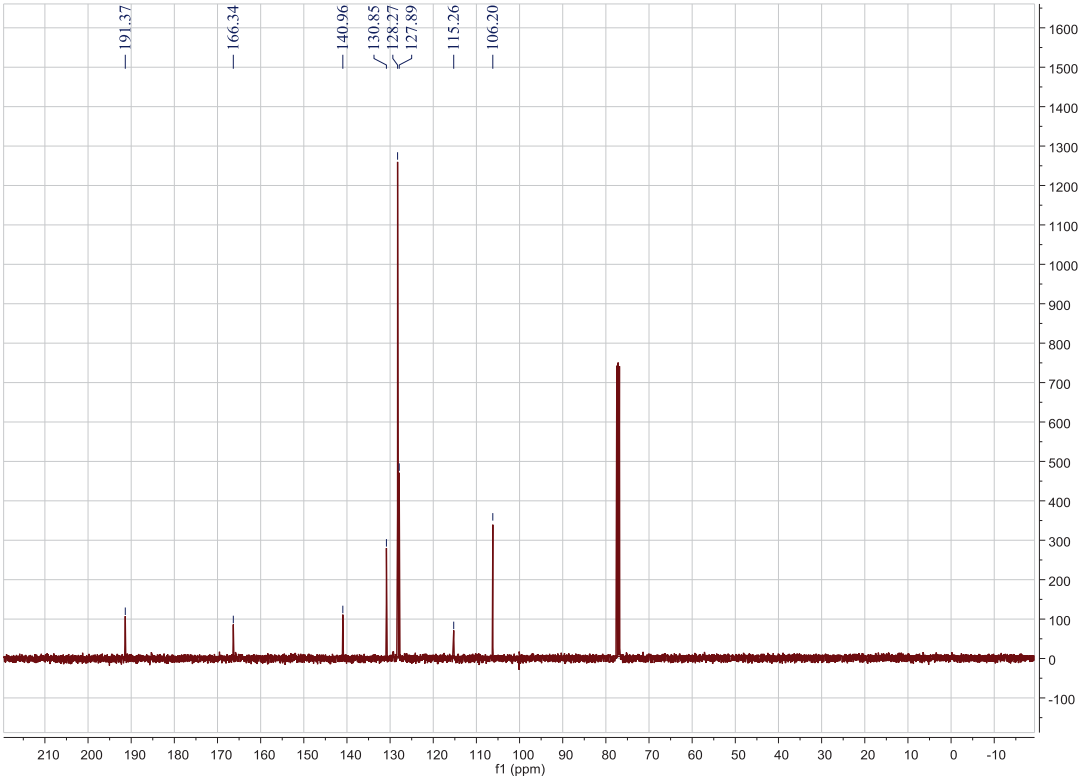


The ^{13}C NMR spectrum of 2-amino-*N*-phenylthiophene-3-carboxamide

2-Amino-3-benzoylthiophene (**5e**, Table 5, Entry 5)

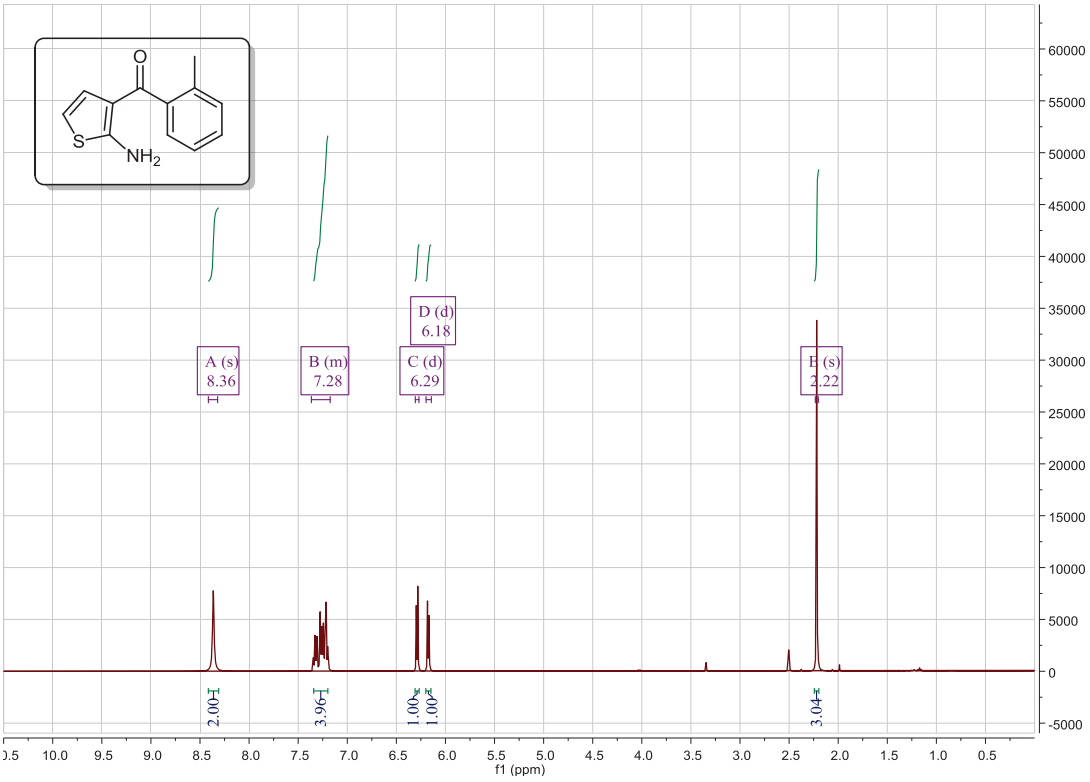


The ^{1}H NMR spectrum of 2-amino-3-benzoylthiophene

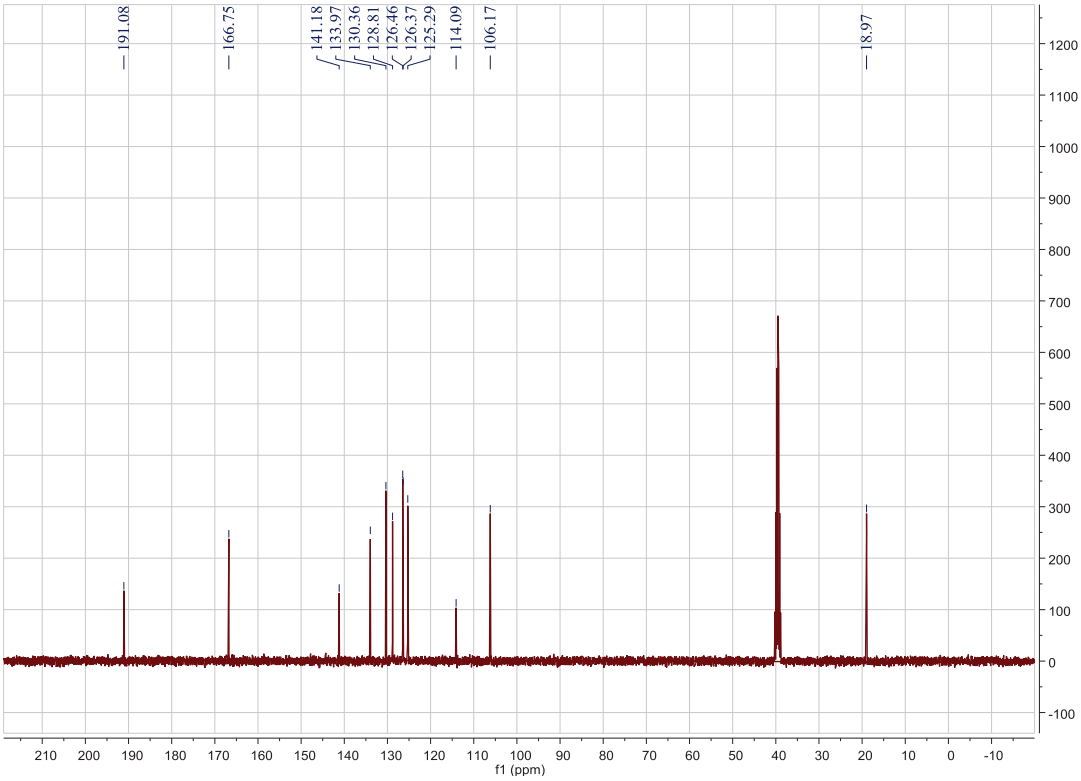


The ^{13}C NMR spectrum of 2-amino-3-benzoylthiophene

2-Amino-3-(2-methylbenzoyl)thiophene (**5f**, Table 5, Entry 6)



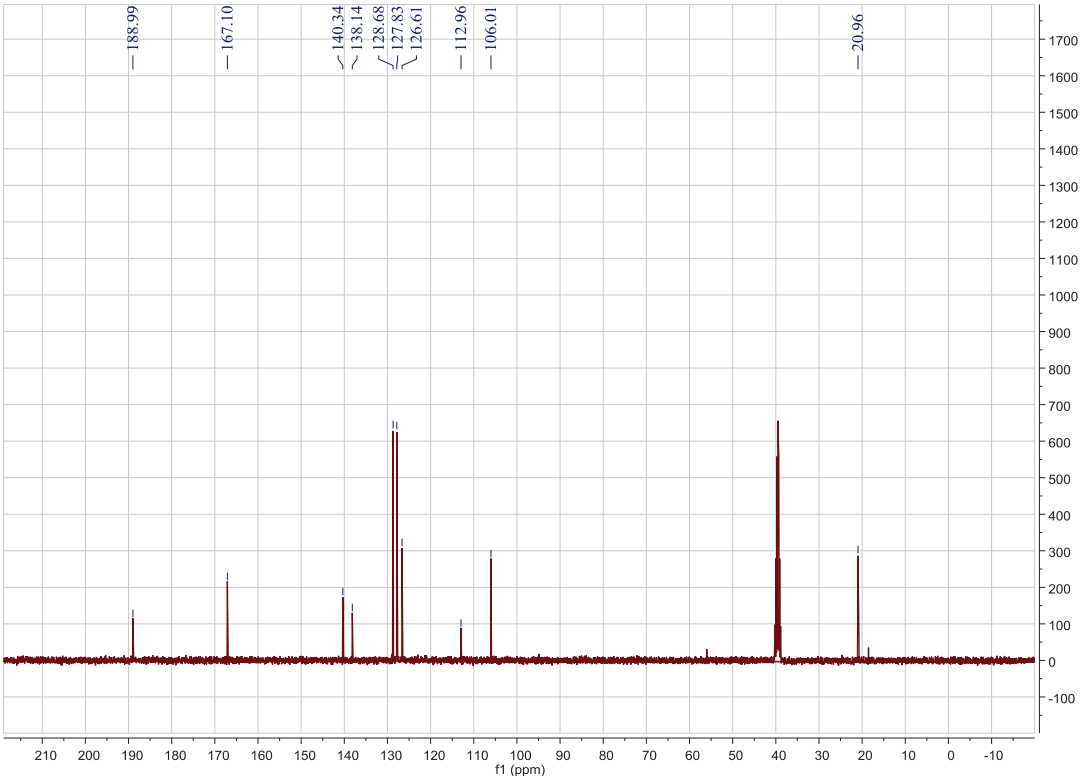
The ^{1}H NMR spectrum of 2-amino-3-(2-methylbenzoyl)thiophene



The ^{13}C NMR spectrum of 2-amino-3-(2-methylbenzoyl)thiophene

2-Amino-3-(4-methylbenzoyl)thiophene (**5g**, Table 5, Entry 7)

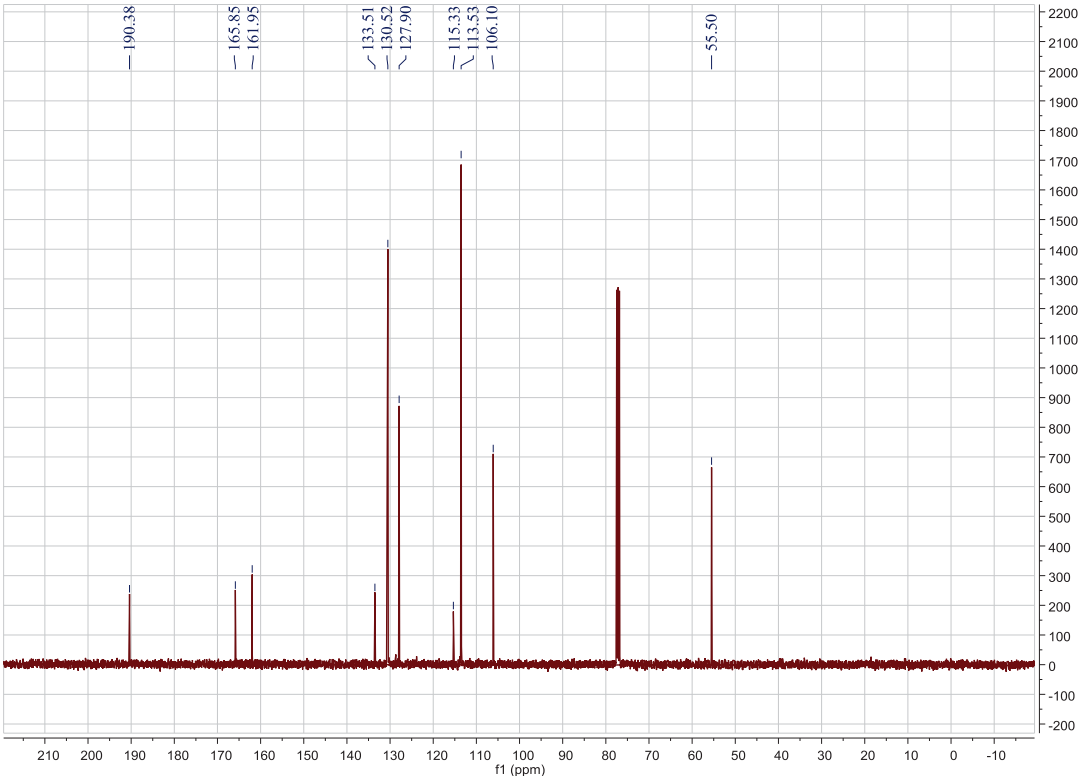
The ^{1}H NMR spectrum of 2-amino-3-(4-methylbenzoyl)thiophene



The ^{13}C NMR spectrum of 2-amino-3-(4-methylbenzoyl)thiophene

2-Amino-3-(4-methoxybenzoyl)thiophene (**5h**, Table 5, Entry 8)

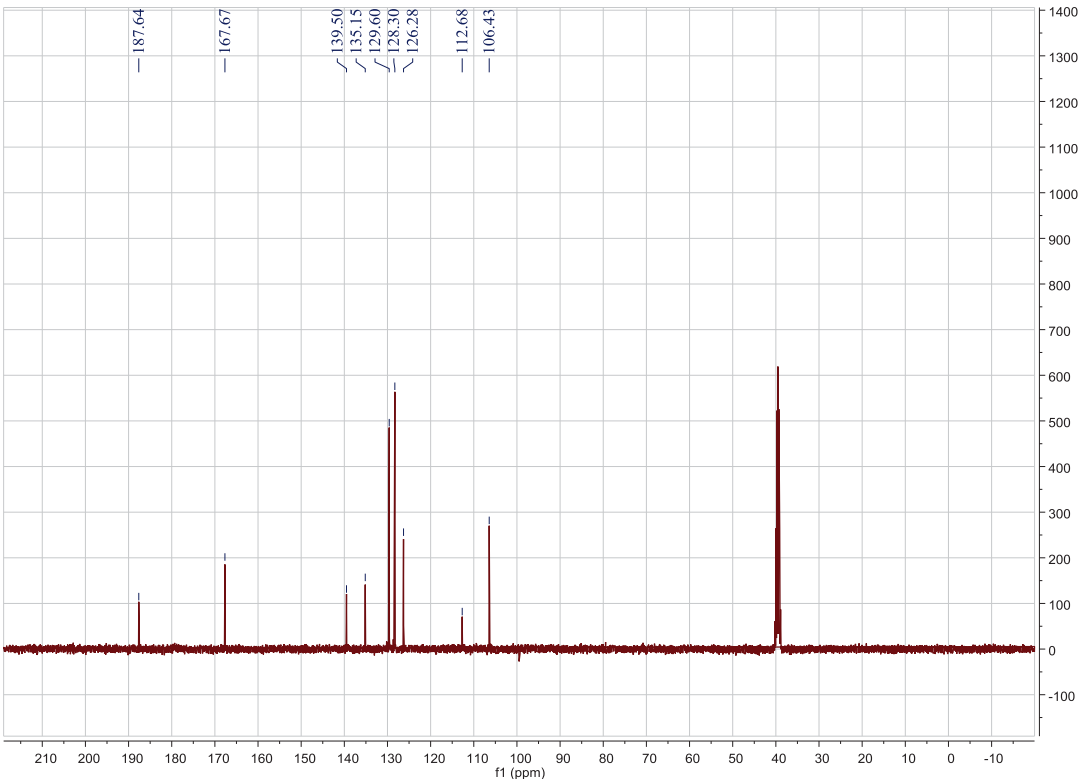
The ^{1}H NMR spectrum of 2-amino-3-(4-methoxybenzoyl)thiophene



The ^{13}C NMR spectrum of 2-amino-3-(4-methoxybenzoyl)thiophene

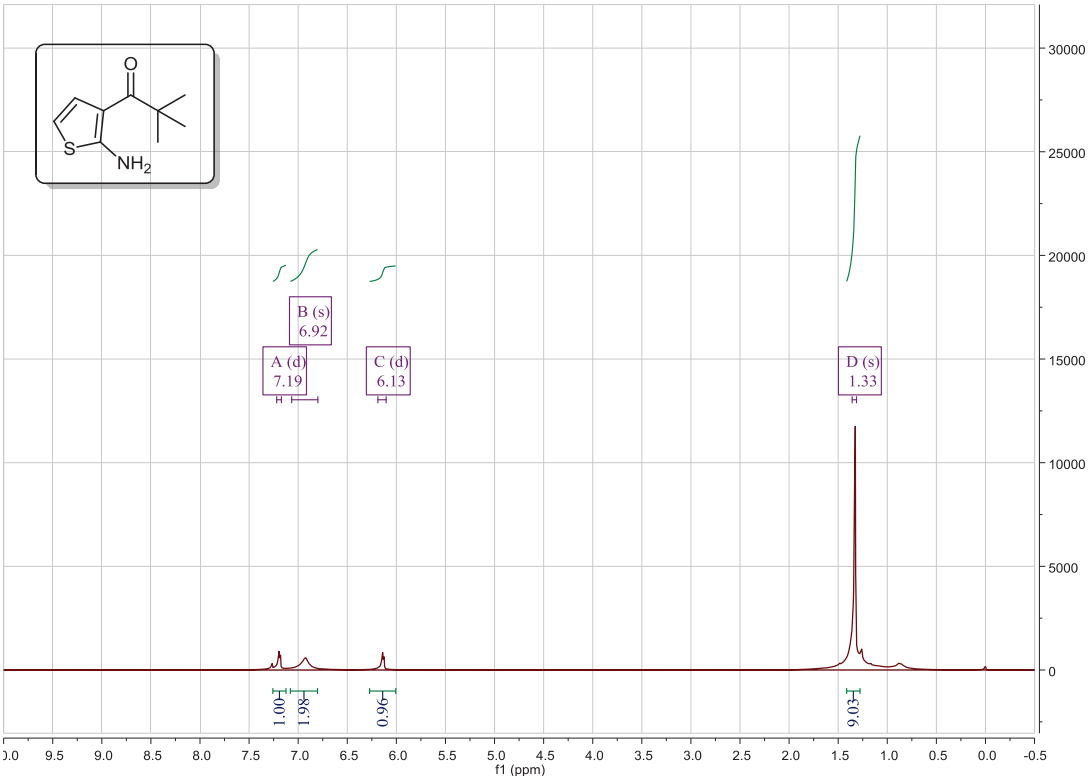
2-Amino-3-(4-chlorobenzoyl)thiophene (**5i**, Table 5, Entry 9)

The ^{1}H NMR spectrum of 2-amino-3-(4-chlorobenzoyl)thiophene

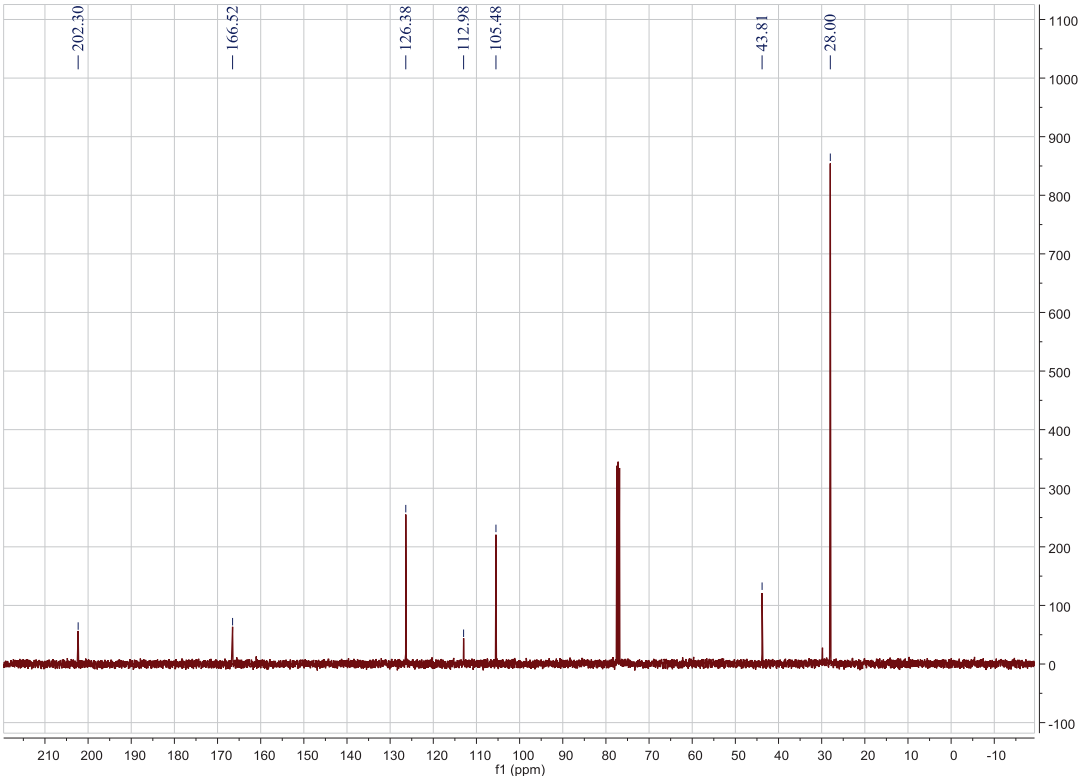


The ^{13}C NMR spectrum of 2-amino-3-(4-chlorobenzoyl)thiophene

2-Amino-3-(2,2-dimethylpropanoyl)thiophene (5j, Table 5, Entry 10)

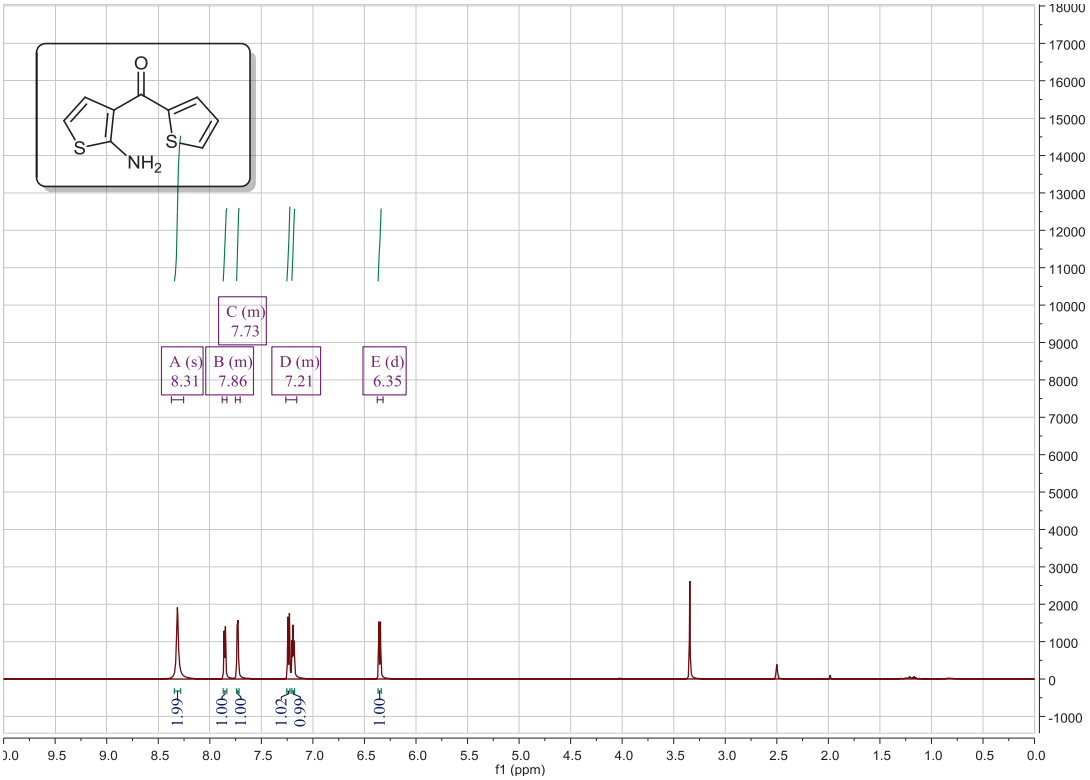


The ^{1}H NMR spectrum of 2-amino-3-(2,2-dimethylpropanoyl)thiophene

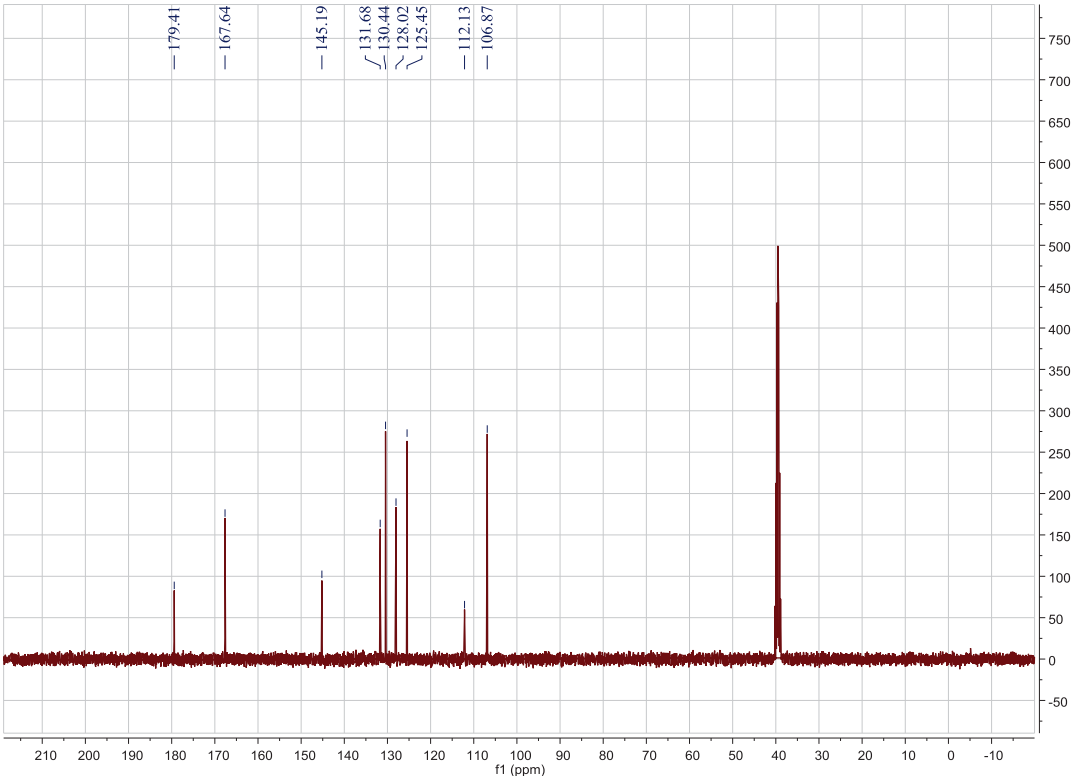


The ^{13}C NMR spectrum of 2-amino-3-(2,2-dimethylpropanoyl)thiophene

2-Amino-3-(2-thiophenoyl)thiophene (**5k**, Table 5, Entry 11)

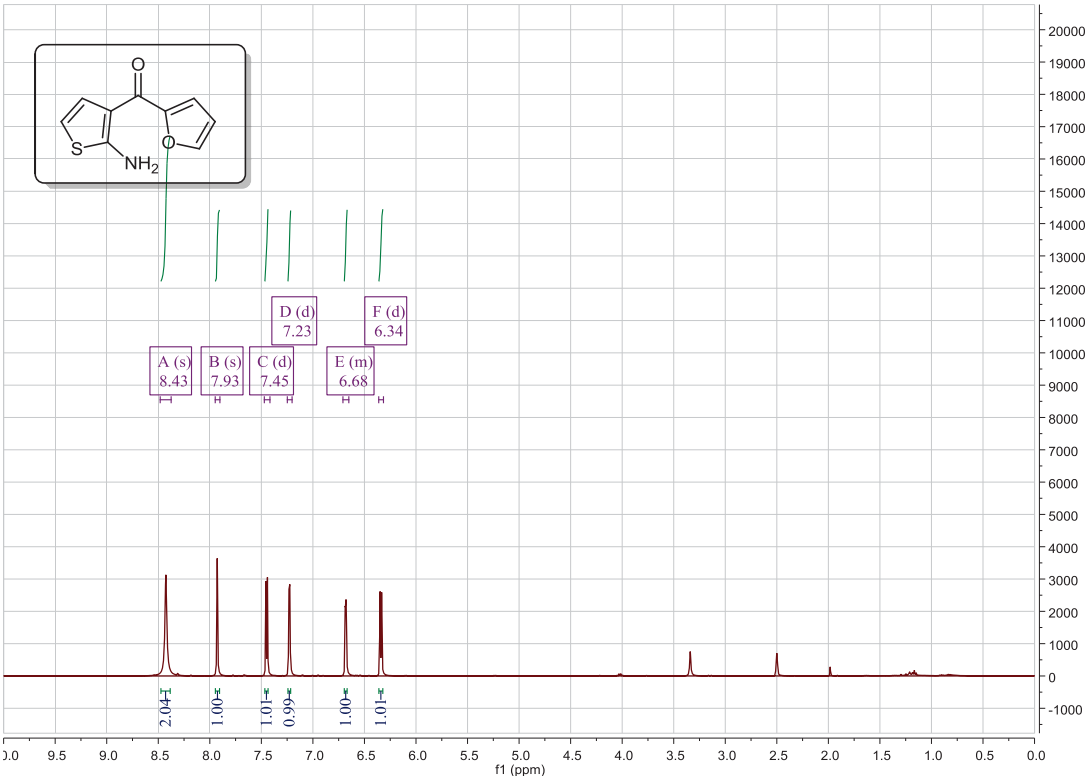


The ^{1}H NMR spectrum of 2-amino-3-(2-thiophenoyl)thiophene

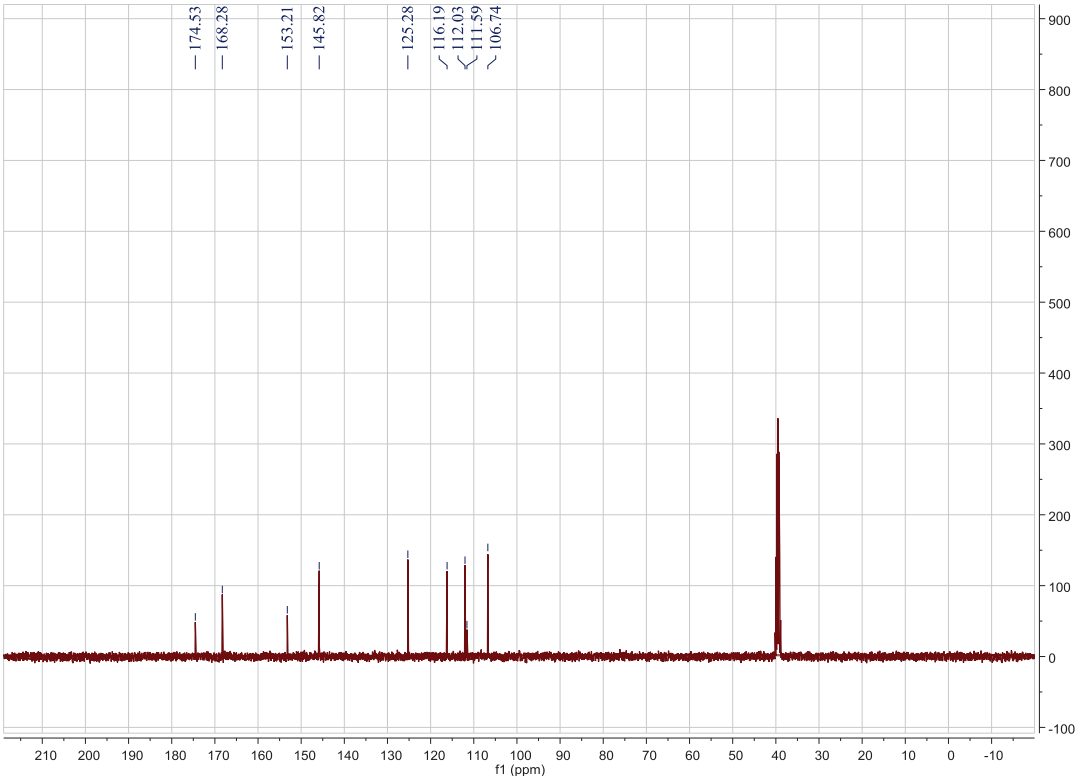


The ^{13}C NMR spectrum of 2-amino-3-(2-thiophenoyl)thiophene

2-Amino-3-(2-furoyl)thiophene (**5l**, Table 5, Entry 12)

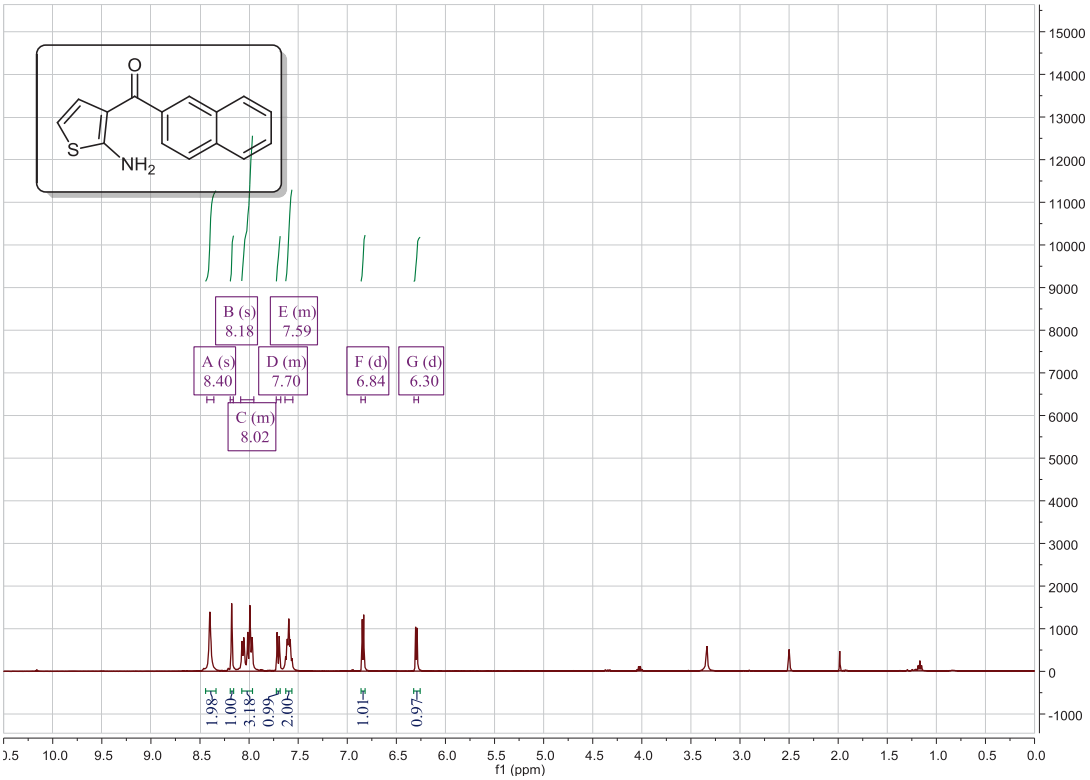


The ^{1}H NMR spectrum of 2-amino-3-(2-furoyl)thiophene

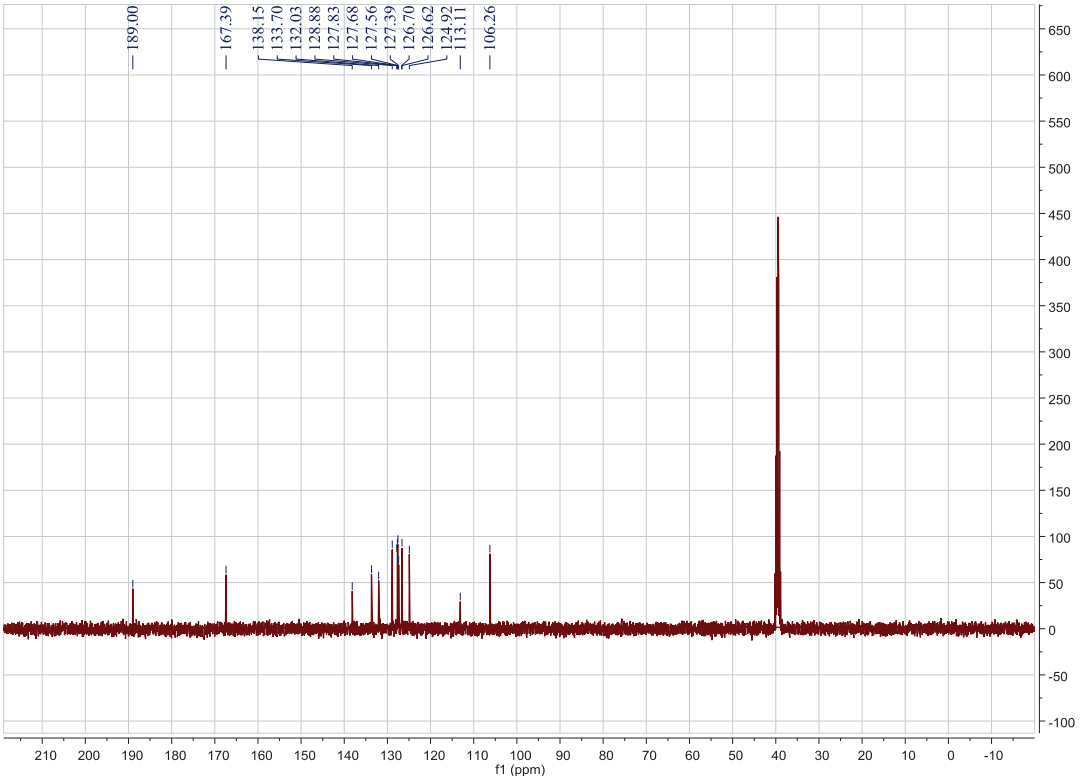


The ^{13}C NMR spectrum of 2-amino-3-(2-furoyl)thiophene

2-Amino-3-(2-naphthoyl)thiophene (**5m**, Table 5, Entry 13)

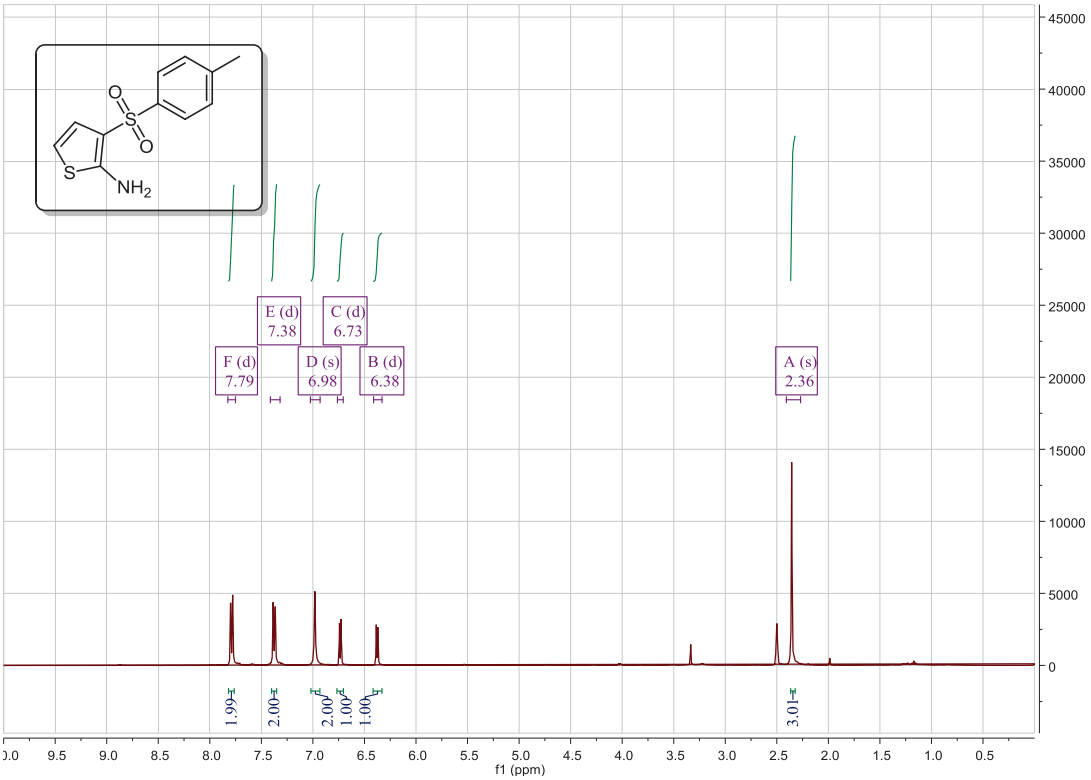


The ^{1}H NMR spectrum of 2-amino-3-(2-naphthoyl)thiophene

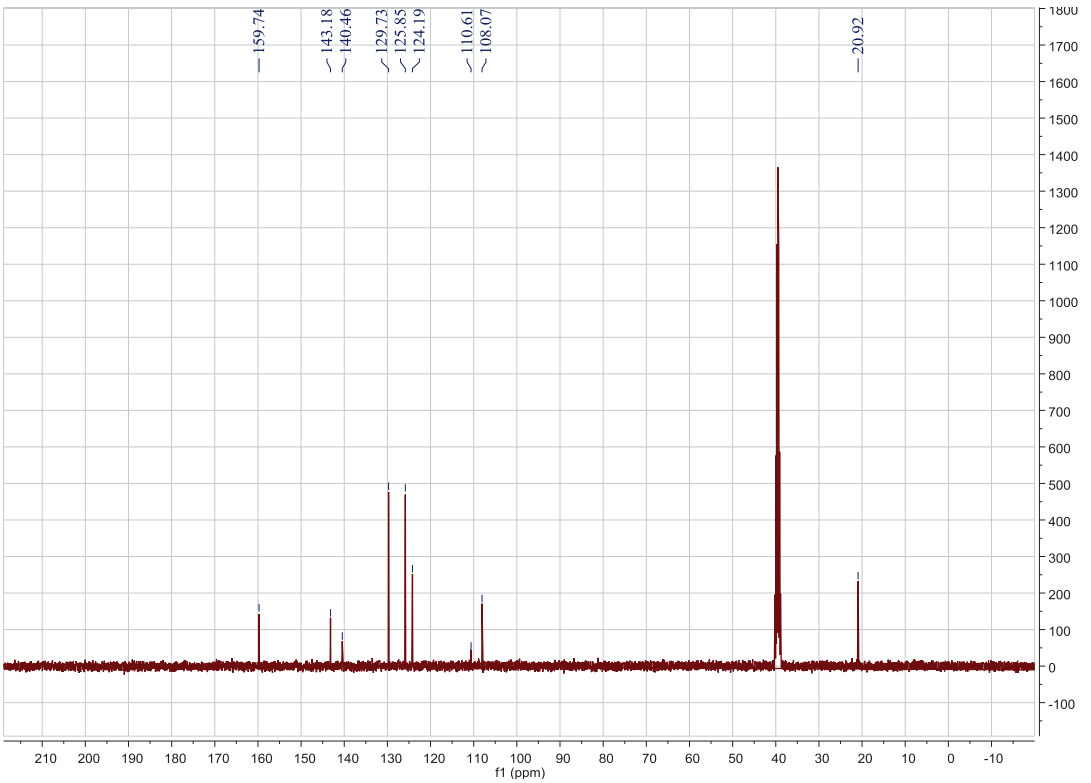


The ^{13}C NMR spectrum of 2-amino-3-(2-naphthoyl)thiophene

2-Amino-3-tosylthiophene (**5n**, Table 5, Entry 14)

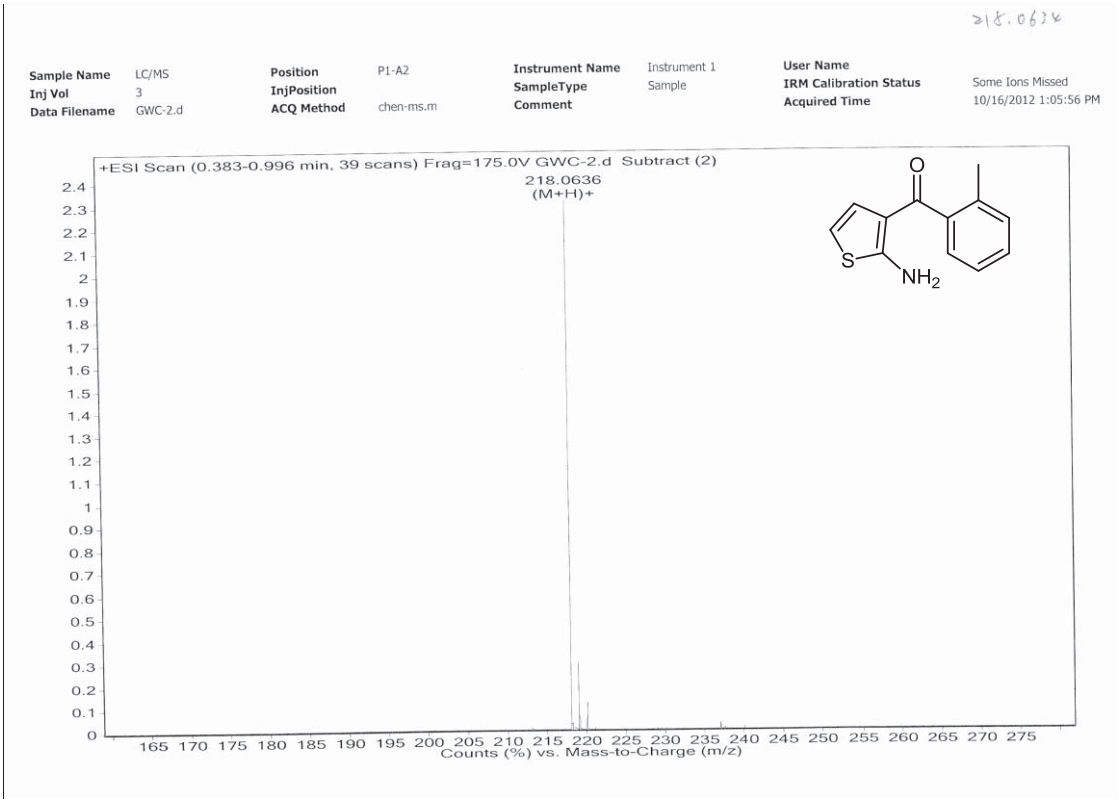


The ^{1}H NMR spectrum of 2-amino-3-tosylthiophene



The ^{13}C NMR spectrum of 2-amino-3-tosylthiophene

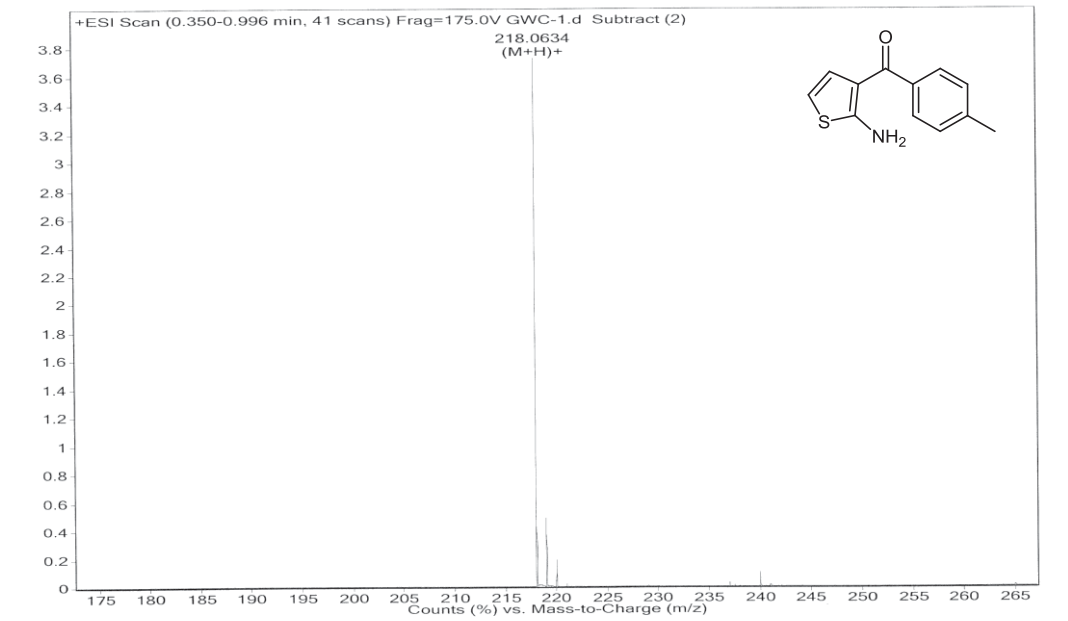
HRMS Spectra



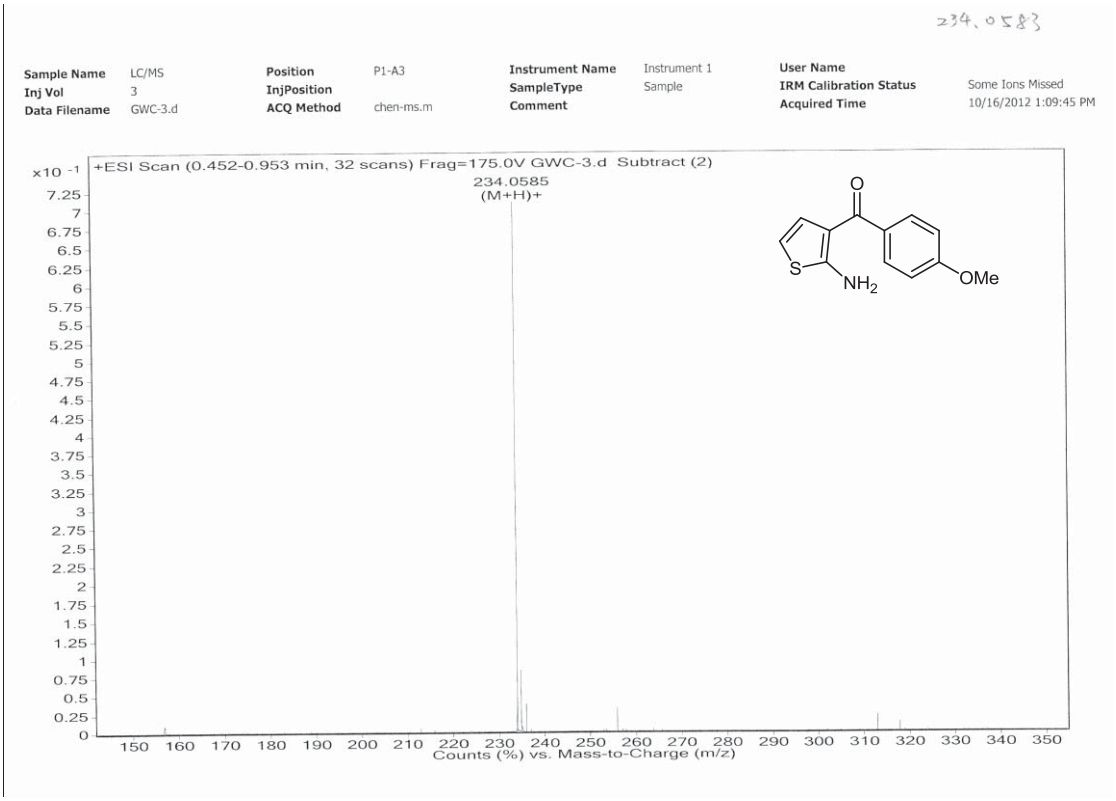
HRMS of 2-amino-3-(2-methylbenzoyl)thiophene (5f)

218.0634

Sample Name	LC/MS	**Position**	P1-A1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	3	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Some Ions Missed
Data Filename	GWC-1.d	**ACQ Method**	chen-ms.m	**Comment**		**Acquired Time**	10/16/2012 1:02:09 PM



HRMS of 2-amino-3-(4-methylbenzoyl)thiophene (5g)



HRMS of 2-amino-3-(4-methoxybenzoyl)thiophene (5h)

210.0042

Sample Name	LC/MS	**Position**	P1-A4	**Instrument Name**	Instrument 1	**User Name**	
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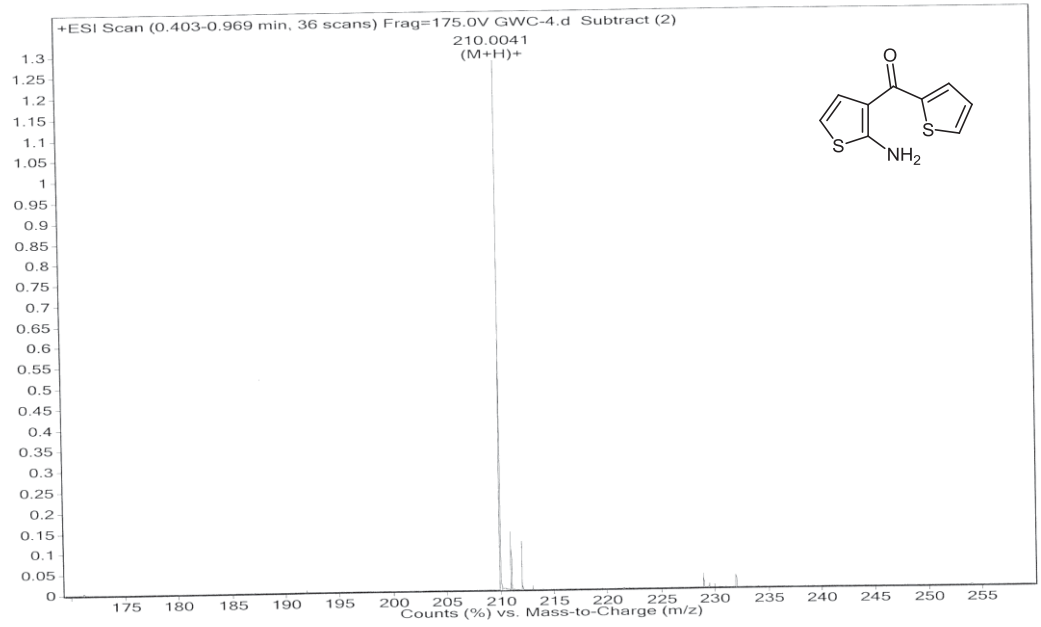

HRMS of 2-amino-3-(2-thiophenoyl)thiophene (5k)

194.0270

Sample Name	LC/MS	**Position**	P1-A5	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	3	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Some Ions Missed
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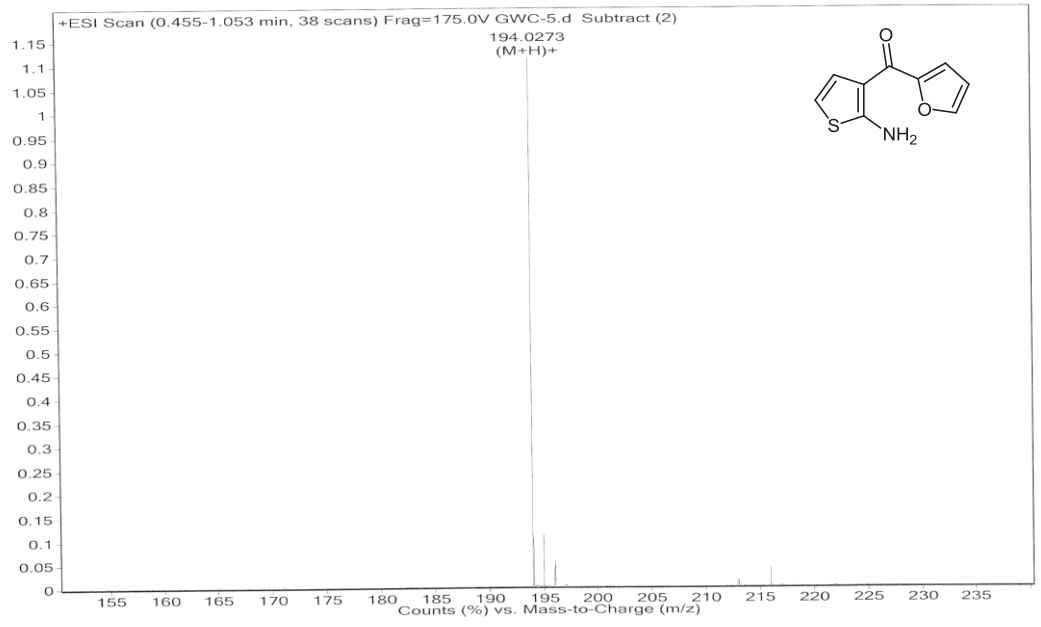

HRMS of 2-amino-3-(2-furoyl)thiophene (5l)

254.0634

Sample Name	LC/MS	**Position**	P1-A6	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	3	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Some Ions Missed
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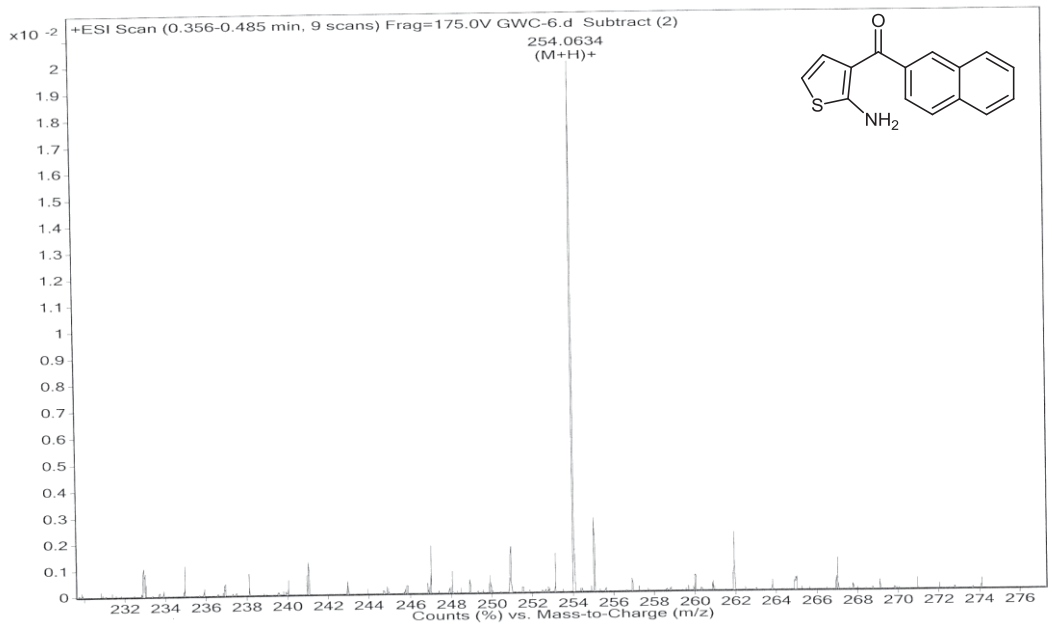

HRMS of 2-amino-3-(2-naphthoyl)thiophene (5m)

Acid exchange capacity of the fiber catalyst:

The acid exchange capacity was calculated according to the amount of acid consumed by P-PANF. Dried P-PANF (0.250 g) was immersed in 20.00 mL of HCl solution (0.100 M) for 6 h. Then the treated fiber was filtered out and washed with water. The concentration of the remaining HCl solution was titrated by 0.100 M NaOH.

Entry	Weight of P-PANF g	The consumed NaOH mL	Average mL	Acid exchange capacity mmol g^{-1}
1	0.250	14.25		
2	0.250	14.20	14.21	2.32
3	0.250	14.20		

The amount of acid consumed by P-PANF = 20.00 mL × 0.100 M – 14.21 mL × 0.100 M = 0.579 mmol

The acid exchange capacity of P-PANF = 0.579 mmol ÷ 0.250 g = 2.32 mmol g^{-1}

The determined acid exchange capacity of P-PANF was 2.32 mmol g^{-1}, indicating that 1.000 g P-PANF contains 1.16 mmol 3-(*N*-methylpiperazinyl)propyl groups (each group has two basic N atoms). Each CN group in PANF reacted with an *N*-methyl-*N*'-(3-aminopropyl)piperazine molecule and get a ΔMW of 158.24 during the amination process.

1 g × 2.32 mmol g^{-1} ÷ 2 × 158.24 g $mmol^{-1}$ = 0.184 g

0.184 g ÷ (1.000 g – 0.184 g) = 22.5 %

This data is in accord with the acid exchange capacity (2.32 mmol g^{-1}).