

Supporting Information

DDQ-Mediated Oxidative Coupling: An Approach to 2,3-Dicyanofuran (Thiophene)

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1. General information

Melting points were obtained in open capillary tubes using a micro melting point apparatus which were uncorrected.

Mass spectra were recorded on TOF mass spectrometer.

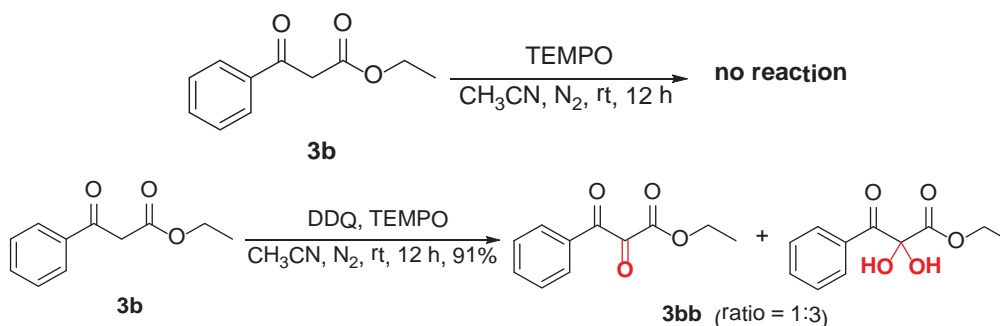
^1H nuclear magnetic resonance (NMR) spectra were recorded using CDCl_3 ($\delta = 7.26$ ppm), $(\text{CD}_3)_2\text{SO}$ ($\delta = 2.50$ ppm) and CD_3CN ($\delta = 1.94$ ppm) as solvent at ambient temperature on the 400 MHz spectrometer. Data are presented as follows: Chemical shift (in ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet), coupling constant (J/Hz) and interpretation. **^{13}C NMR** spectra were recorded by broadband spin decoupling for CDCl_3 ($\delta = 77.2$ ppm), $(\text{CD}_3)_2\text{SO}$ ($\delta = 39.5$ ppm) and CD_3CN ($\delta = 118.3$ ppm) at ambient temperatures on 100 MHz spectrometer. Chemical shift values are reported in ppm on the scale.

Infrared spectra were recorded as thin film. Resonance frequencies are given in wave numbers (cm^{-1}).

TLC (Thin layer chromatograms) was performed using commercially prepared 100-400 mesh silica gel plates, and visualisation was effected at 254 or 365 nm.

Unless otherwise noted, all reagents and solvents were used as purchased. Acetonitrile was dried and distilled from calcium hydride under nitrogen. Toluene and tetrahydrofuran were dried and distilled from sodium/benzophenone under nitrogen. 3-oxo-3-phenylpropanenitrile,^[1] 3-oxobutanenitrile,^[1] *N,N*-dimethyl-3-oxo-3-phenylpropanethioamide^[2] were prepared following the literature procedures.

2. Procedure for radical trapping experiments



A solution of carbonyl compound **3b** (39 mg, 0.2 mmol) and TEMPO (95 mg, 0.6 mmol) in dry CH_3CN (2 mL) was treated with 2, 3-dichloro-5, 6-dicyanobenzoquinone (DDQ) (137 mg, 0.6 mmol) at room temperature under an atmosphere of N_2 . Then the resulting mixture was stirred until the reaction was complete, as judged by TLC. The solvent was evaporated to dryness to give **3bb** (ratio = 1:3, determined by ^1H NMR spectroscopy) as a light yellow oil in 91% yield (38 mg).

after column chromatography (100-200 mesh silica gel, petroleum ether/ethyl acetate = 5:1 as eluent). The observed characterisation data (^1H and ^{13}C NMR spectra, HRMS and IR) are consistent with that previously reported in the literature.^[3]

3. Procedure for EPR experiments^[4]

Procedure for the investigation of the reaction between DDQ and methyl acetoacetate (**1a**) or methyl 3-(4-chlorophenyl)-3-oxopropanoate (**3h**) in CH_3CN by EPR

DDQ (70.0 mg, 0.3 mmol) and methyl acetoacetate **1a** (12.0 mg, 0.1 mmol) or methyl 3-(4-chlorophenyl)-3-oxopropanoate **3h** (22.0 mg, 0.1 mmol) were dissolved in dry CH_3CN (1.0 mL). The mixture was stirred at room temperature for 30 minutes, then a 20 μL aliquot was analysed by EPR spectroscopy at room temperature (Figure S1).

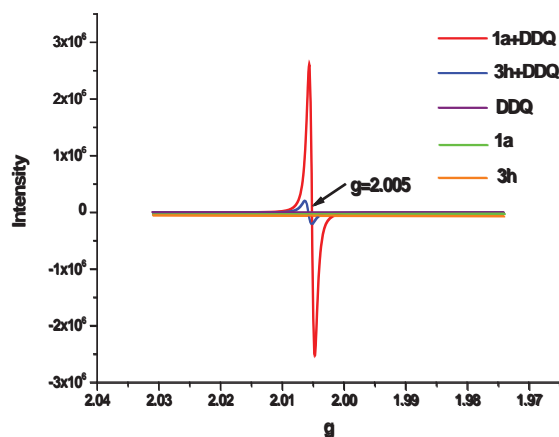


Figure S1. EPR spectra from the reaction between DDQ and methyl acetoacetate (**1a**) or methyl 3-(4-chlorophenyl)-3-oxopropanoate (**3h**) in CH_3CN at room temperature.

As shown in Figure S1, an authentic sample of DDQ, methyl acetoacetate **1a** or 3-(4-chlorophenyl)-3-oxopropanoate **3h** in CH_3CN were detected by EPR spectroscopy, and no signals were observed. However, when methyl acetoacetate **1a** was mixed with DDQ for 30 minutes, a strong signal with a g-factor of 2.005 was clearly detected (Figure S1, red line). This result demonstrates that DDQ reacts with methyl acetoacetate **1a** to produce a radical. To assign this signal, 3-(4-chlorophenyl)-3-oxopropanoate **3h** was subsequently reacted with DDQ instead of **1a** and examined by EPR. A signal was also observed (Figure S1, blue line), for which the g-factor was also 2.005. If this radical originated from the carbonyl compound, different g-factors should be detected when employing different carbonyl compounds. However, identical g-factors for both experiments suggested that the DDQH radical is the likely origin of the signal.^[5]

Procedure for EPR investigation of the reaction between DDQ and methyl acetoacetate (**1a**)

in CH₃CN

DDQ (70.0 mg, 0.3 mmol) and methyl acetoacetate **1a** (12.0 mg, 0.1 mmol) were dissolved in dry CH₃CN (1.0 mL), the mixture was stirred at room temperature for a few minutes, then a 20 μ L aliquot was analysed at room temperature by EPR (Figure S2).

The time dependency of the DDQ-mediated oxidative coupling of methyl acetoacetate **1a** was next monitored by EPR spectroscopy (Figure S2). After 30 minutes a strong signal with g-factor of 2.005 was observed, and a moderate signal was detected at 60 minutes. This agrees with the possibility that the signal gradually disappears as DDQH₂ and the desired product accumulates.

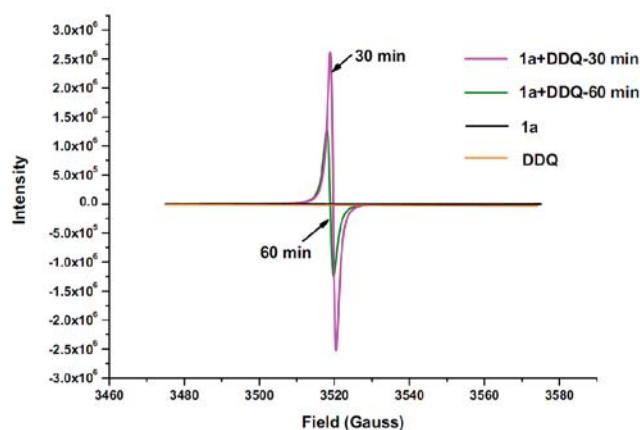
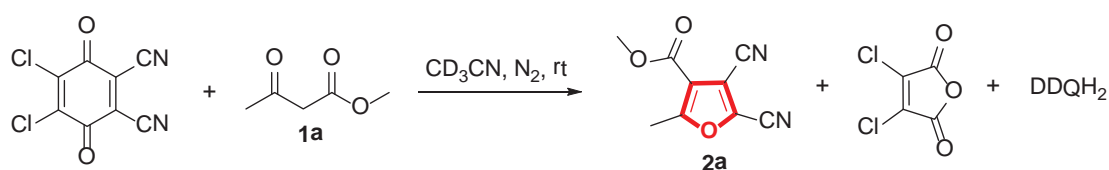


Figure S2. EPR spectra from the reaction between methyl acetoacetate **1a** and DDQ in CH₃CN at room temperature.

4. Procedure for NMR experiments



1a (12.0 mg, 0.1 mmol) was added to a solution of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (70.0 mg, 0.3 mmol) in dry CD₃CN (1.0 mL) at room temperature under an atmosphere of N₂. Then the resulting mixture was stirred and monitored by NMR spectroscopy with time (Figure S3-S10).

A series of *in-situ* NMR spectroscopy experiments are shown in the following figures

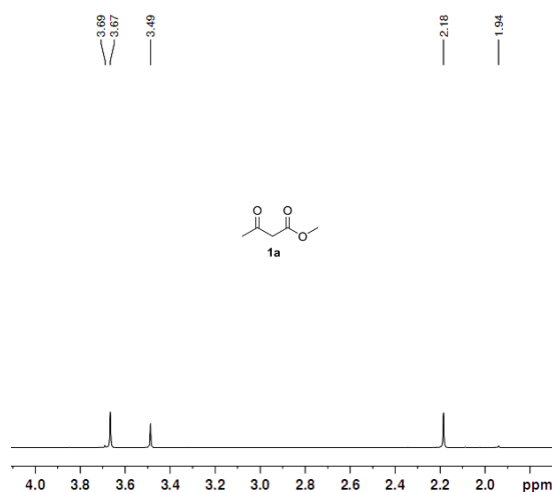


Figure S3. ^1H NMR spectroscopy of **1a**.

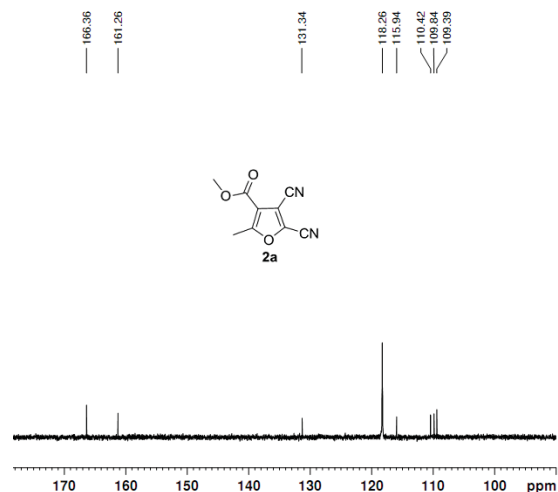


Figure S4. ^{13}C NMR spectroscopy of **2a**.

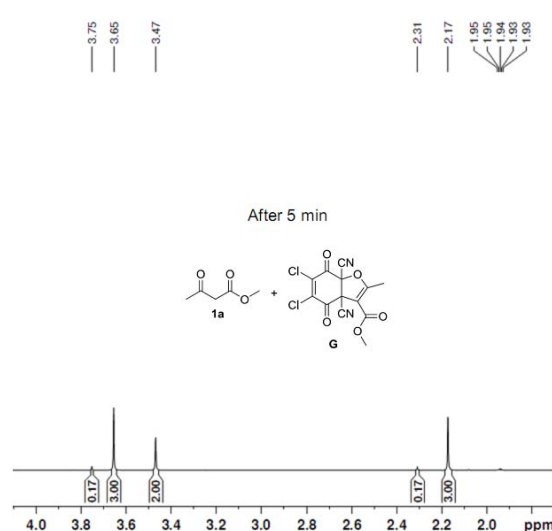


Figure S5. After 5 min.

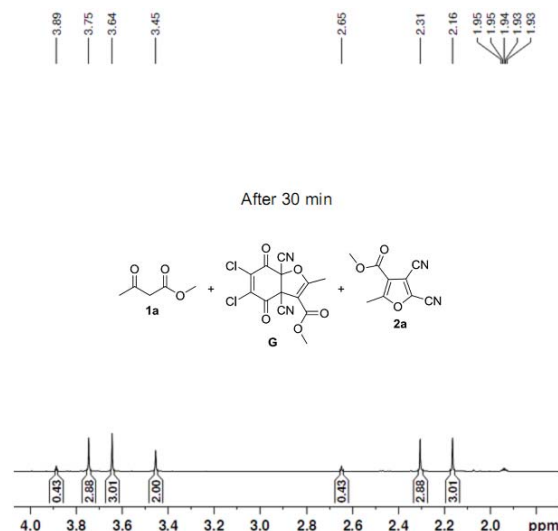


Figure S6. After 30 min.

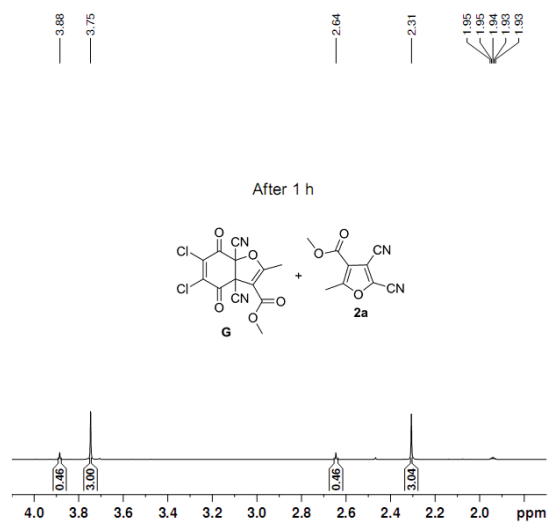
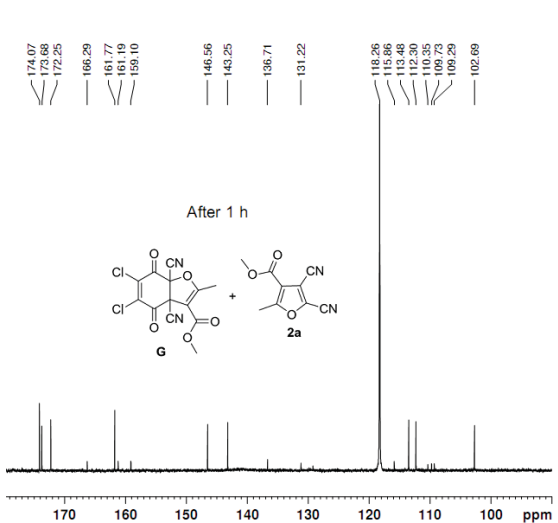


Figure S7. After 1h.



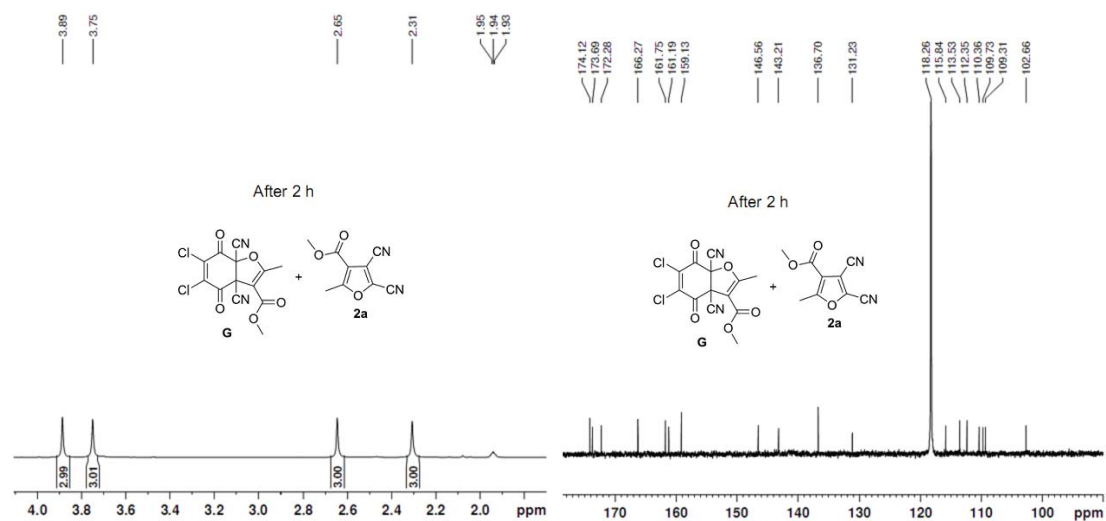


Figure S8. After 2h.

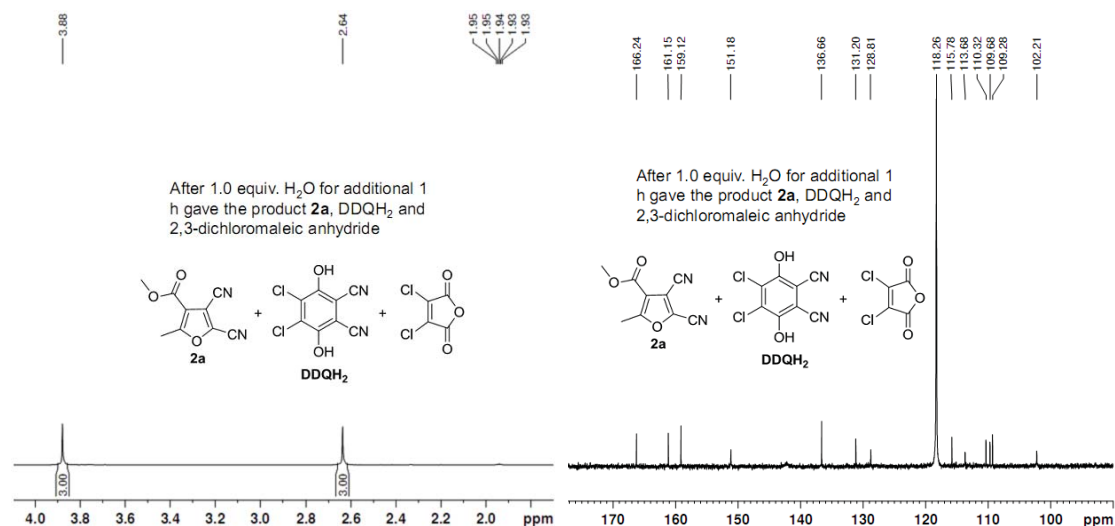


Figure S9. After 1.0 equiv. H₂O for additional 1 h.

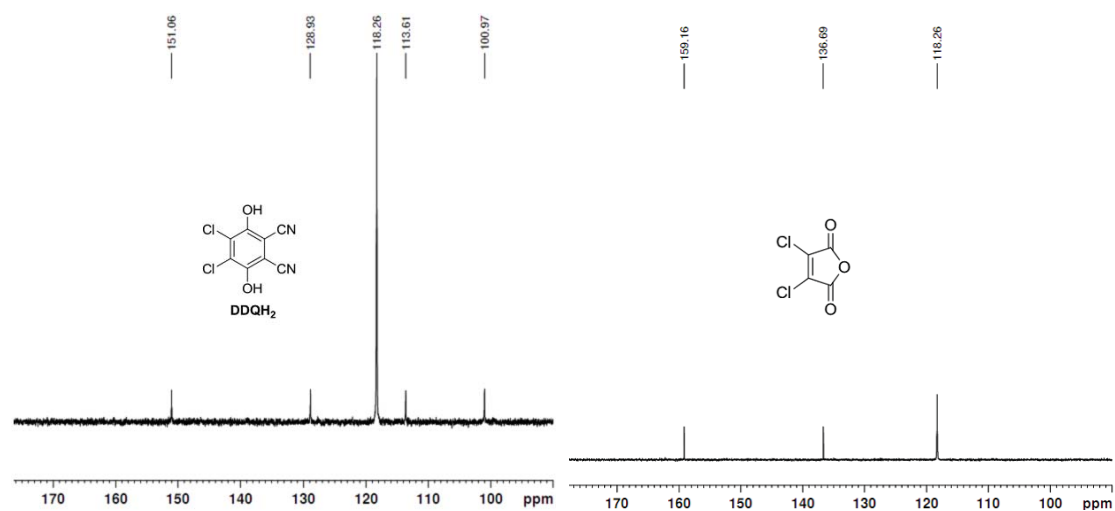
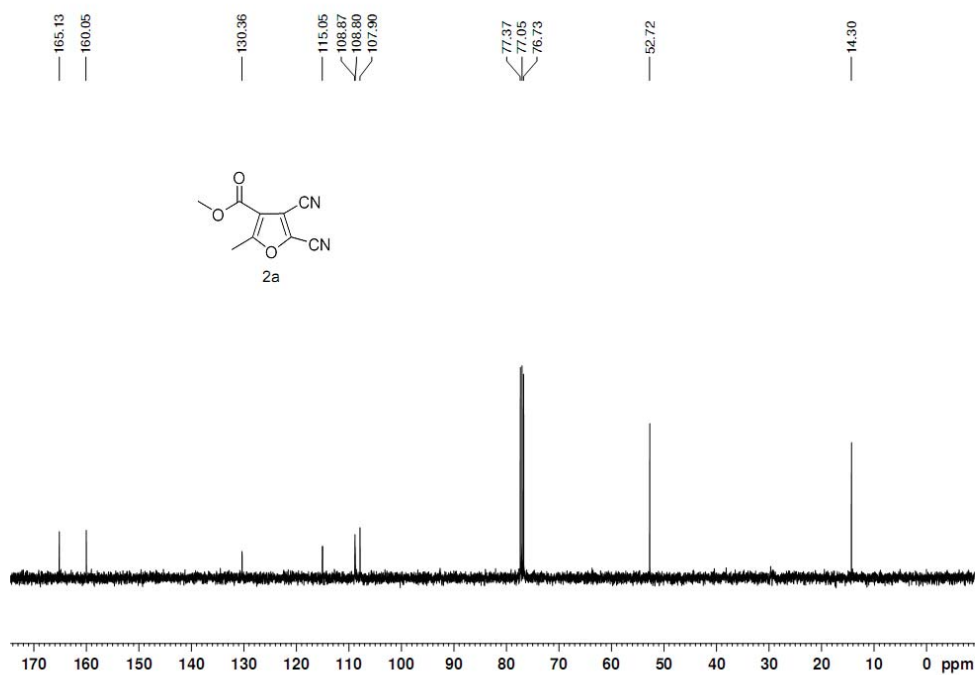
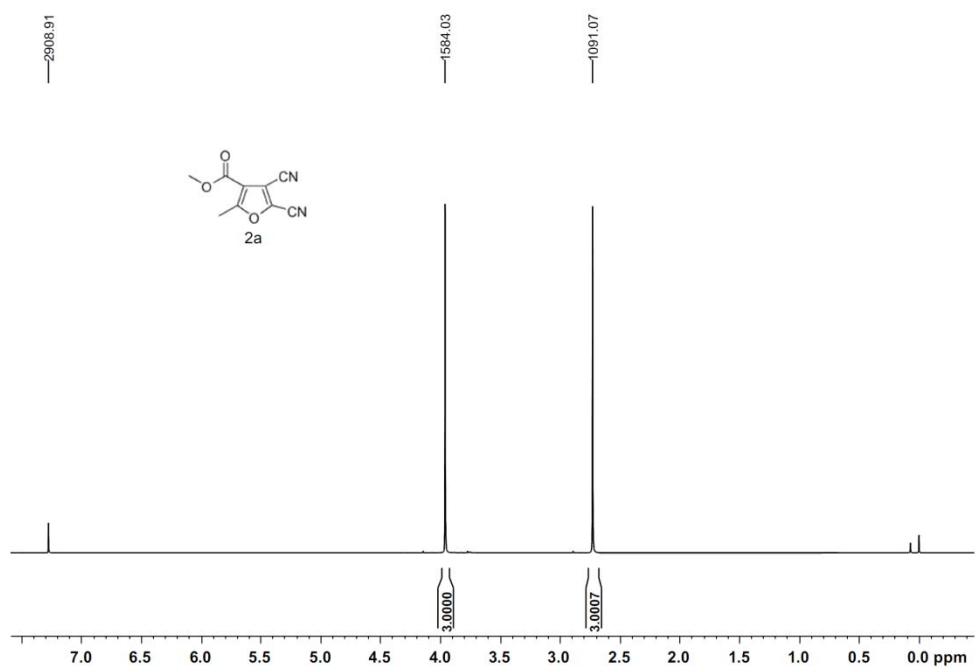
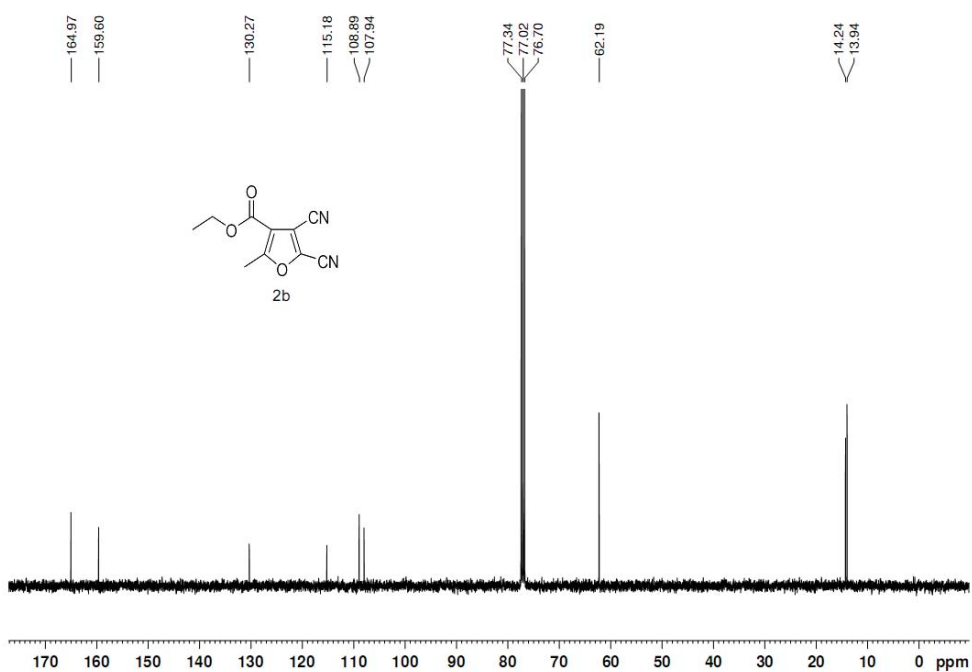
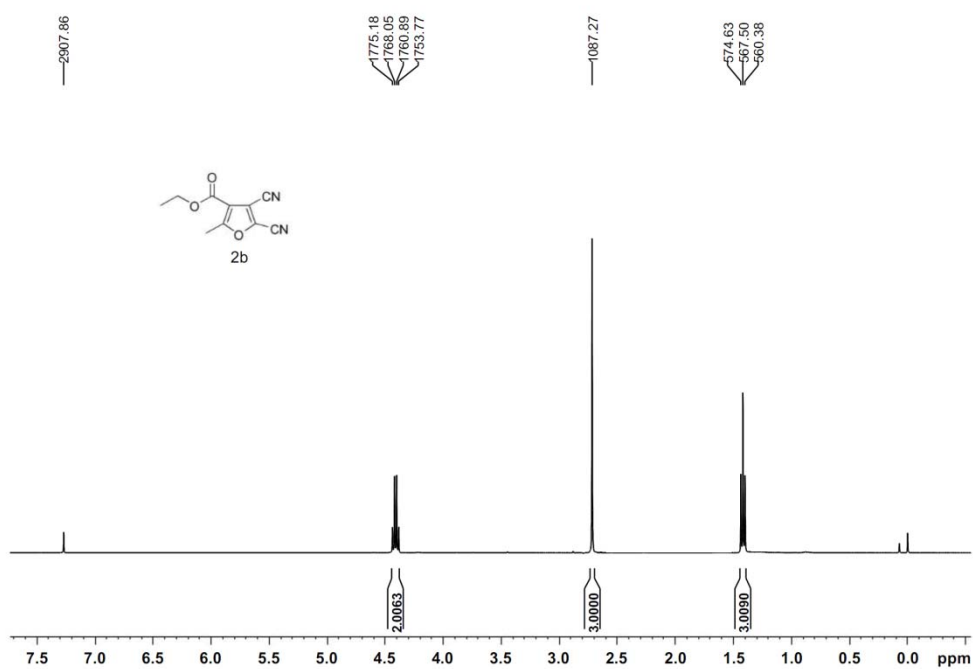


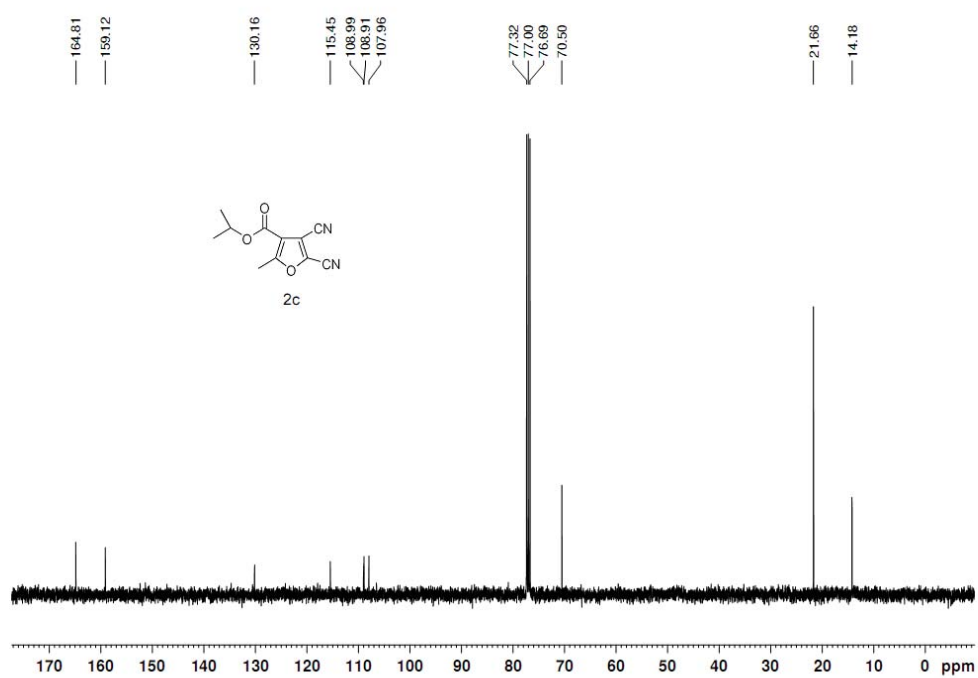
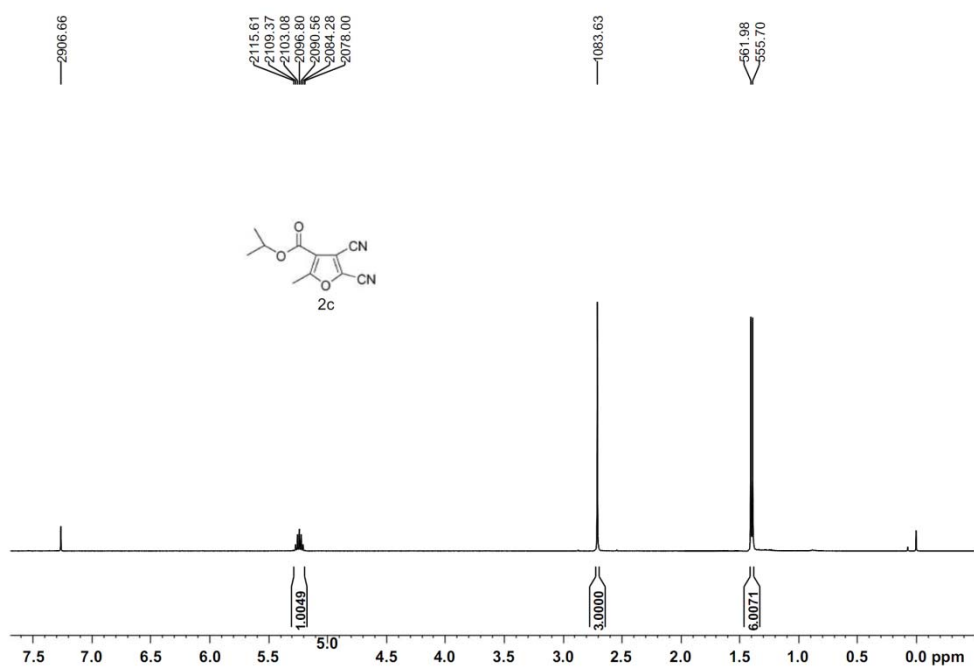
Figure S10. ¹³C NMR spectroscopy of DDQH₂ and 2,3-dichloromaleic anhydride.

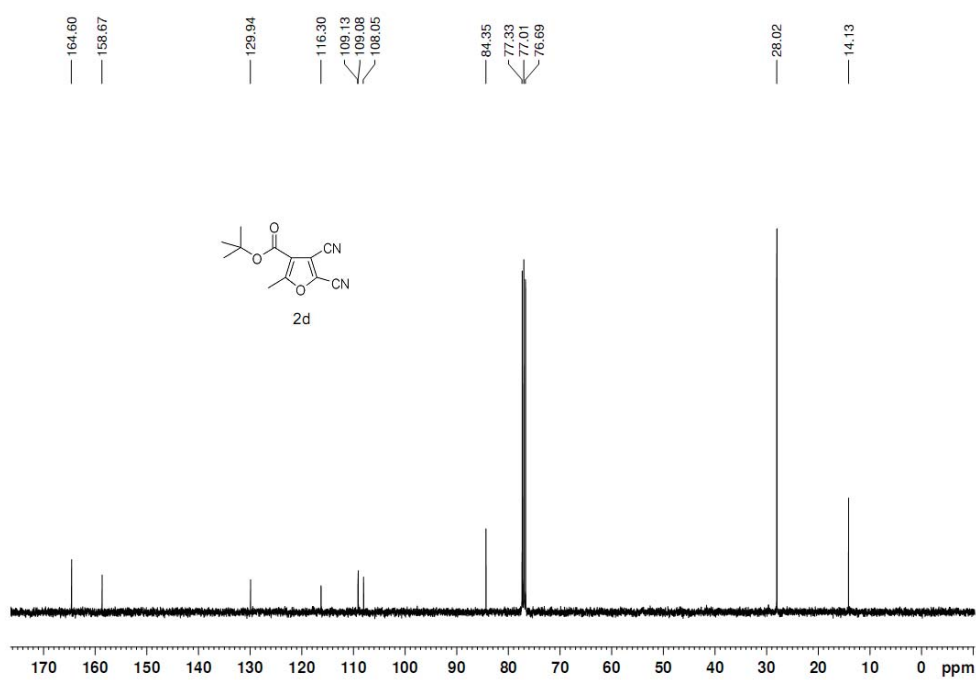
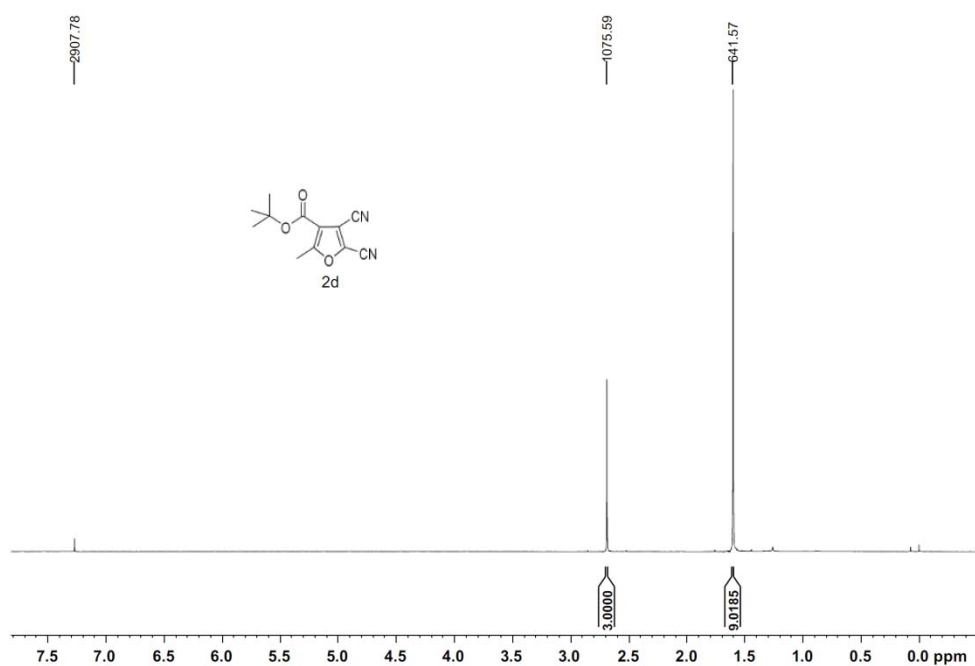
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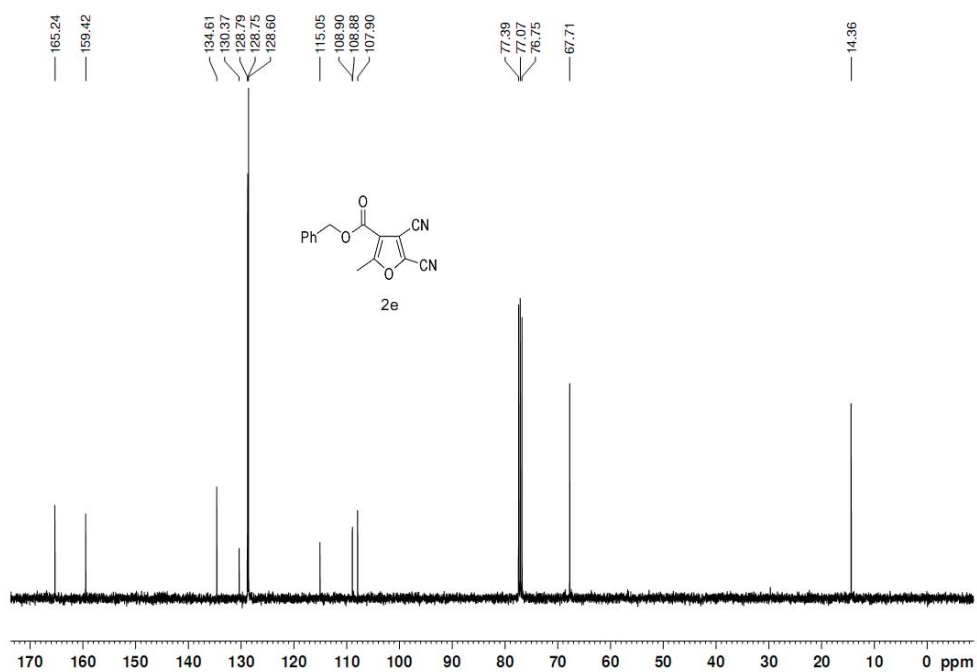
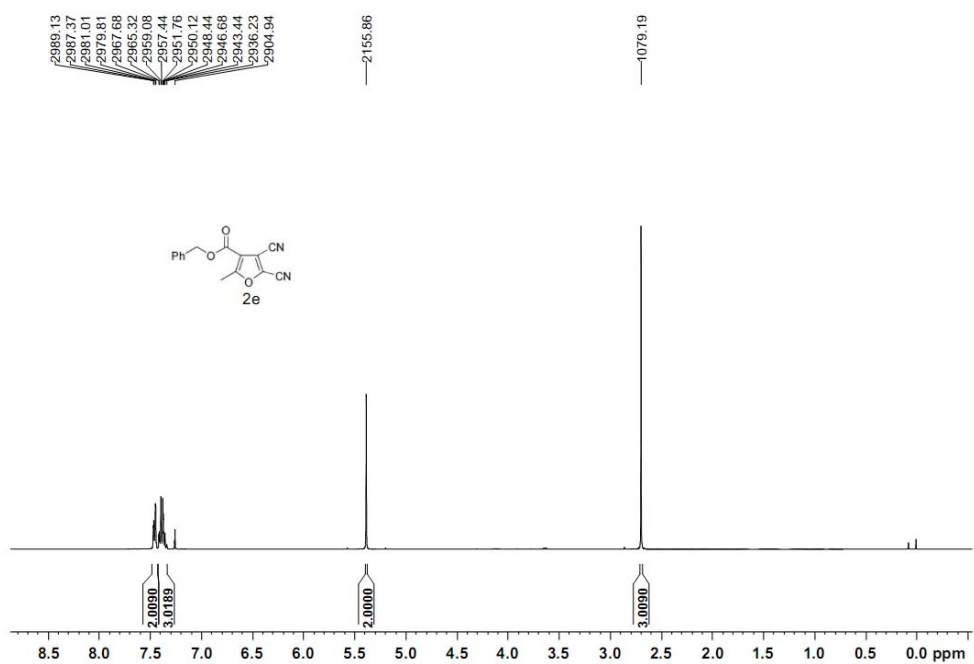
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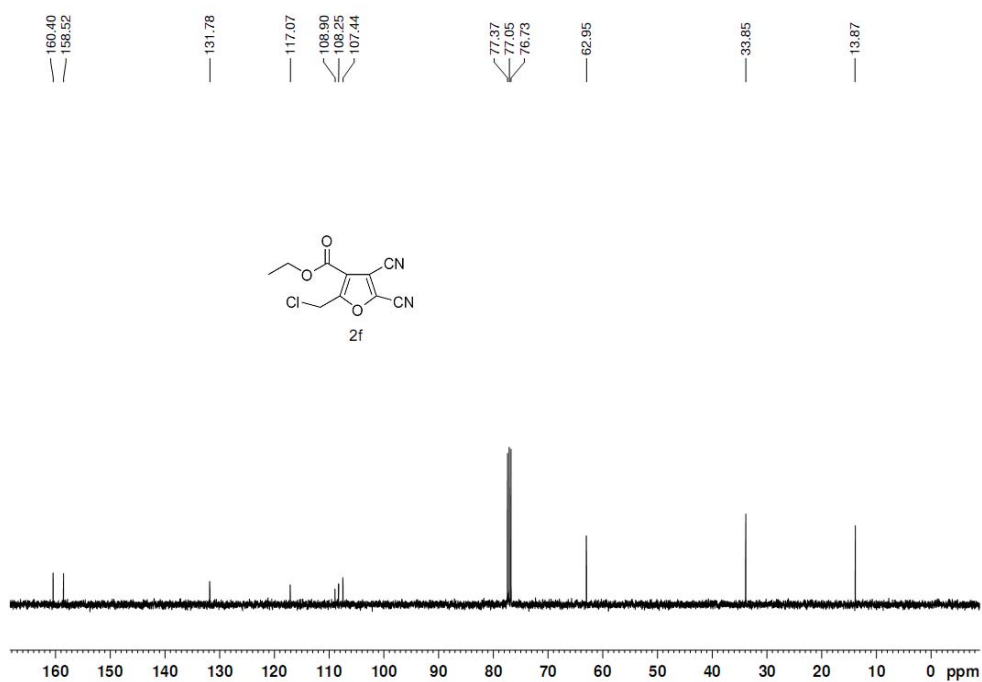
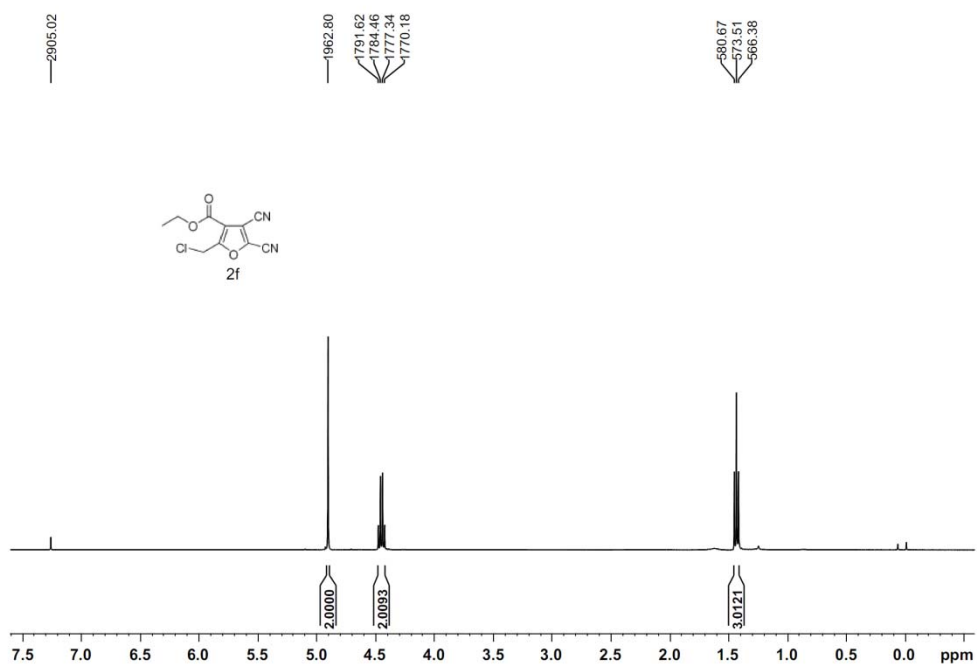


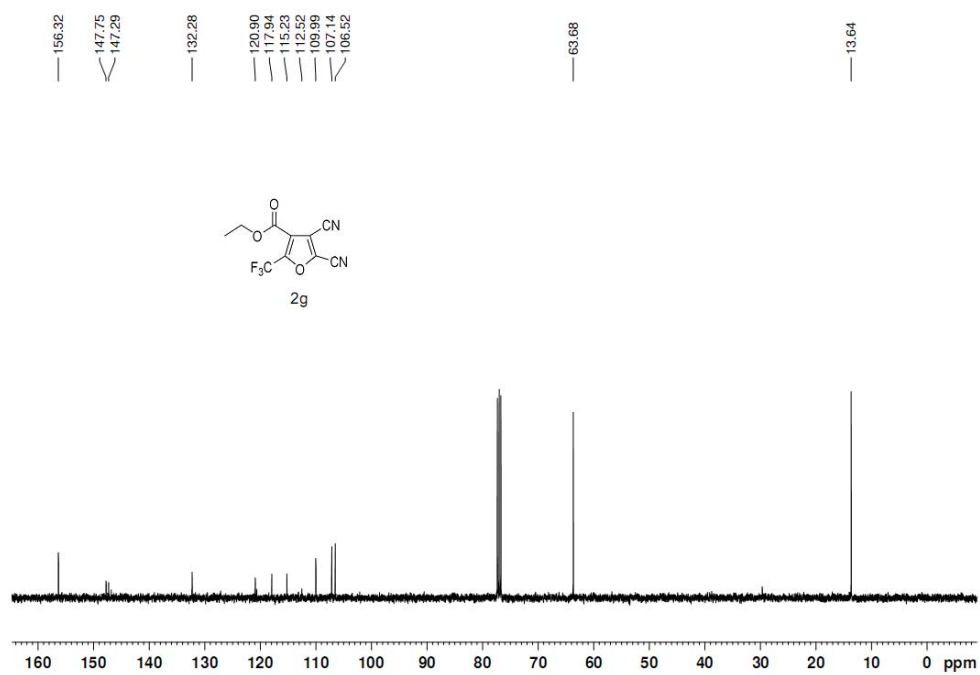
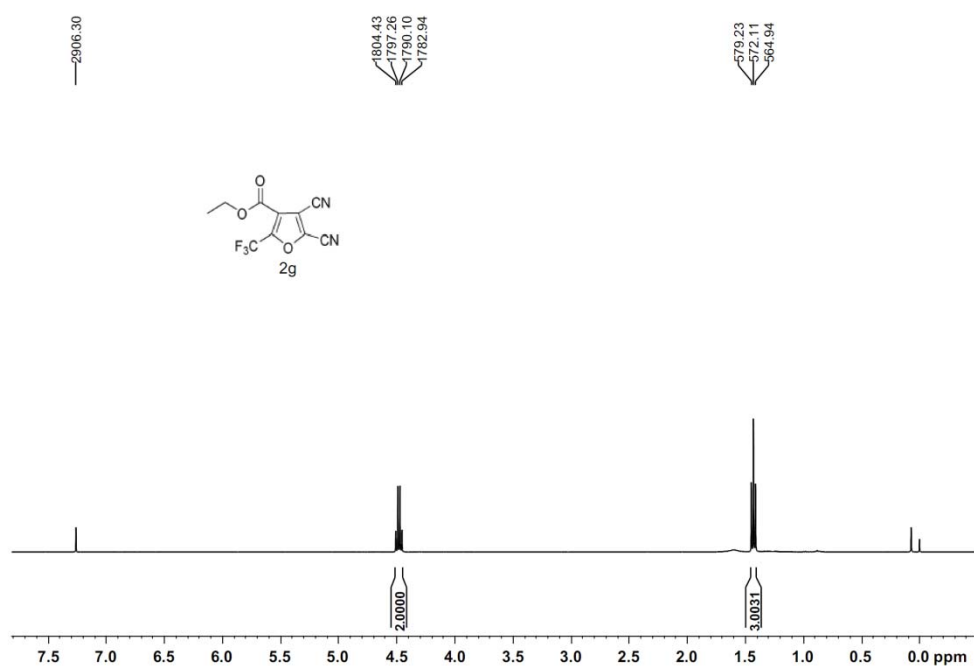


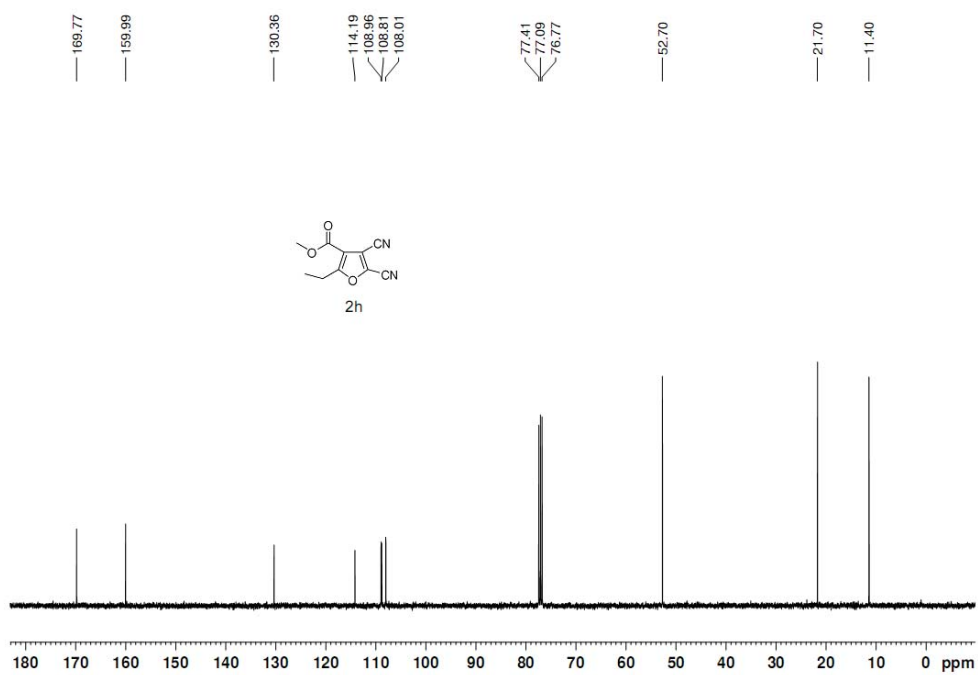
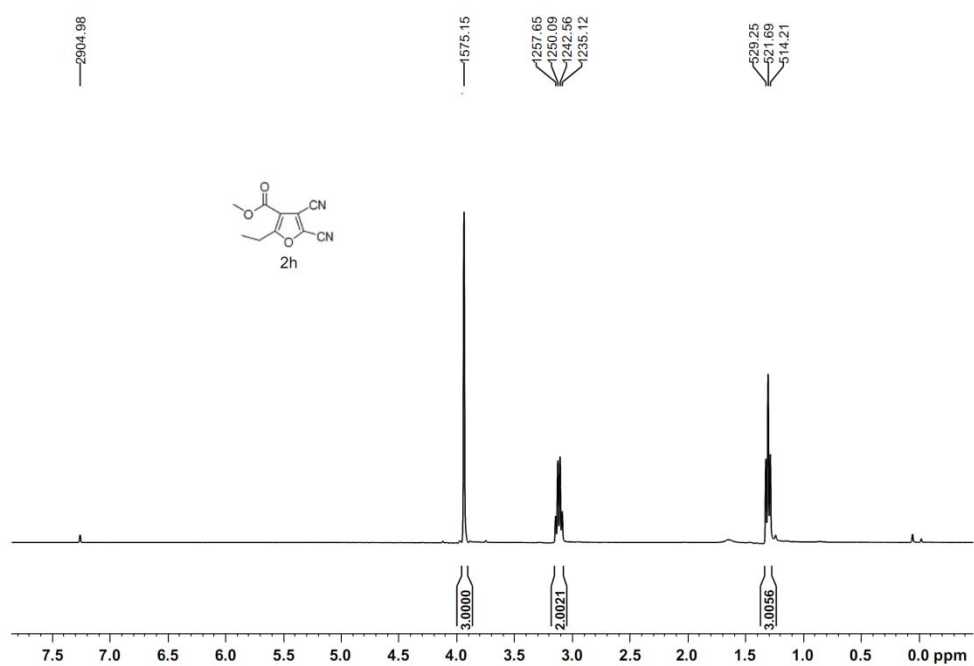


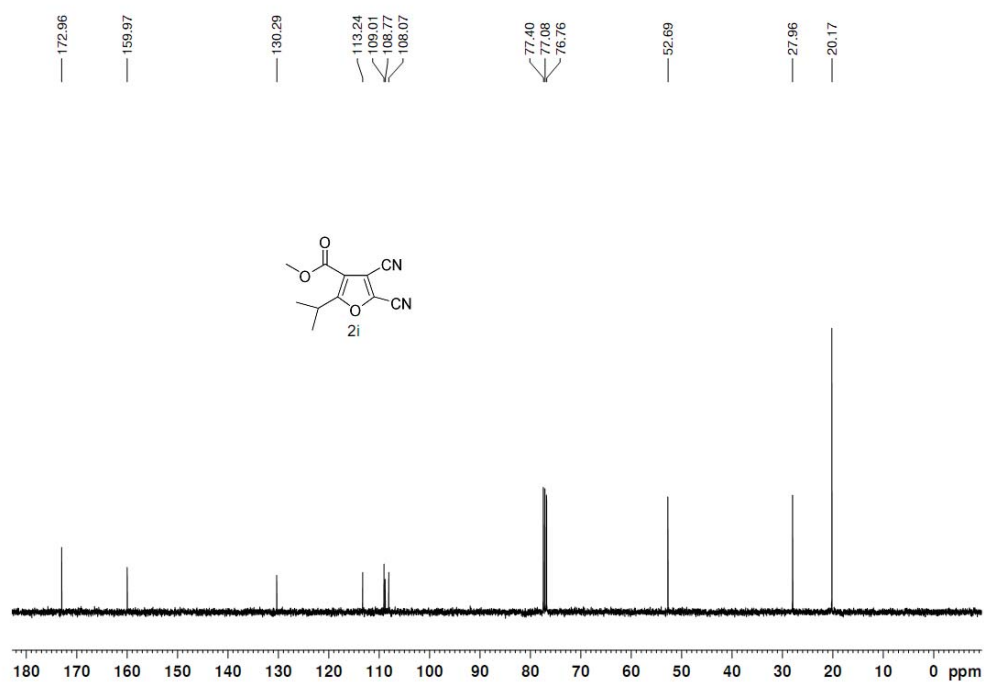
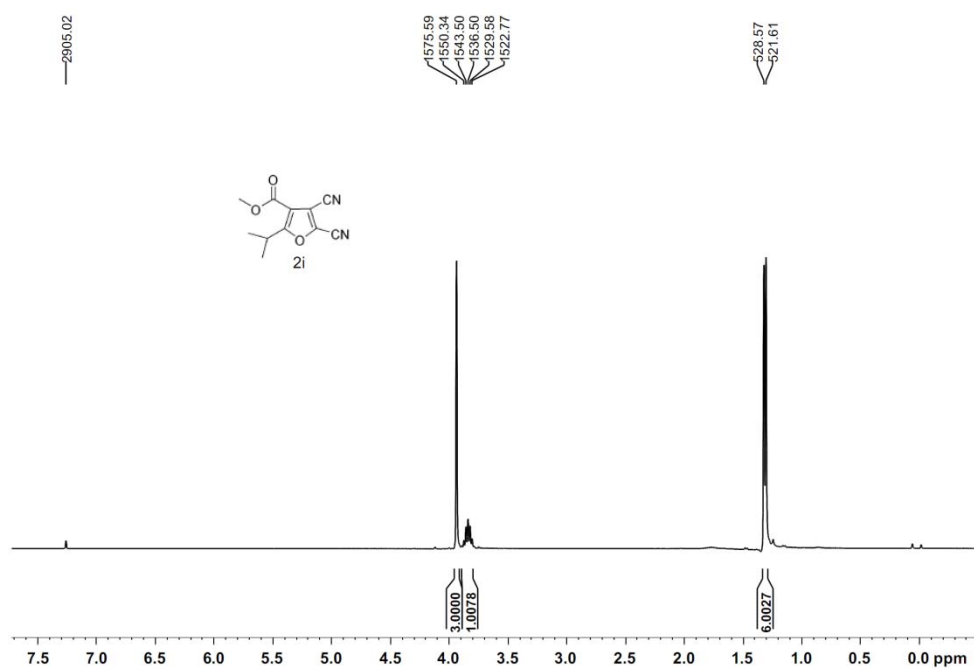


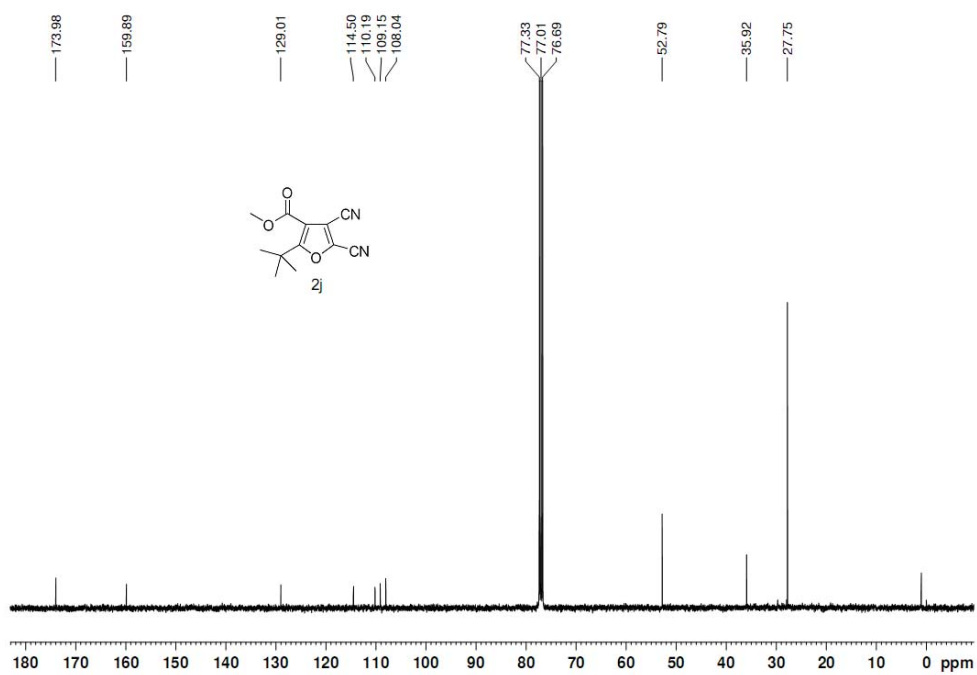
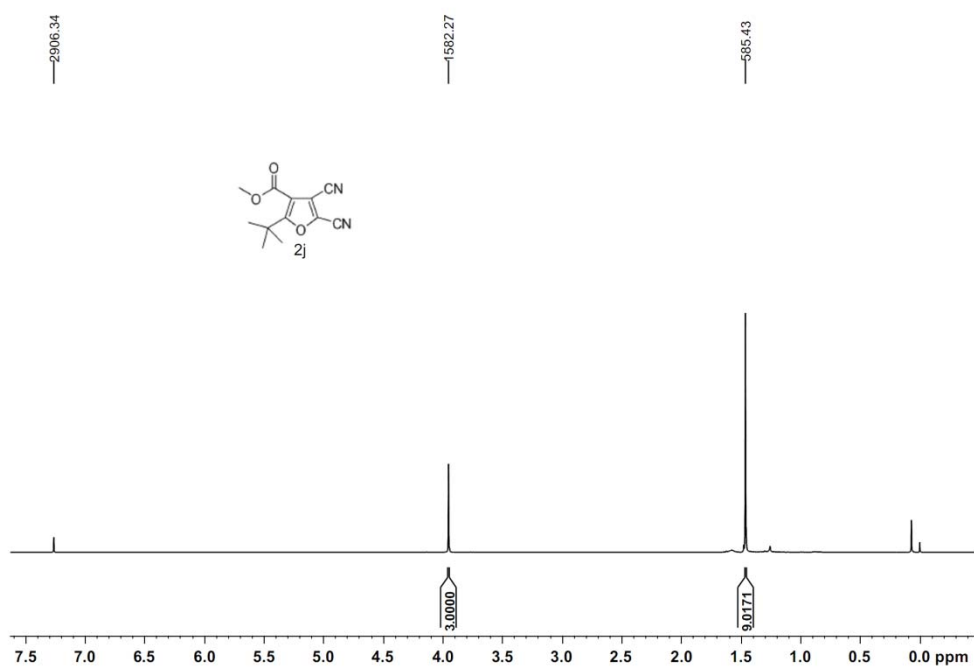


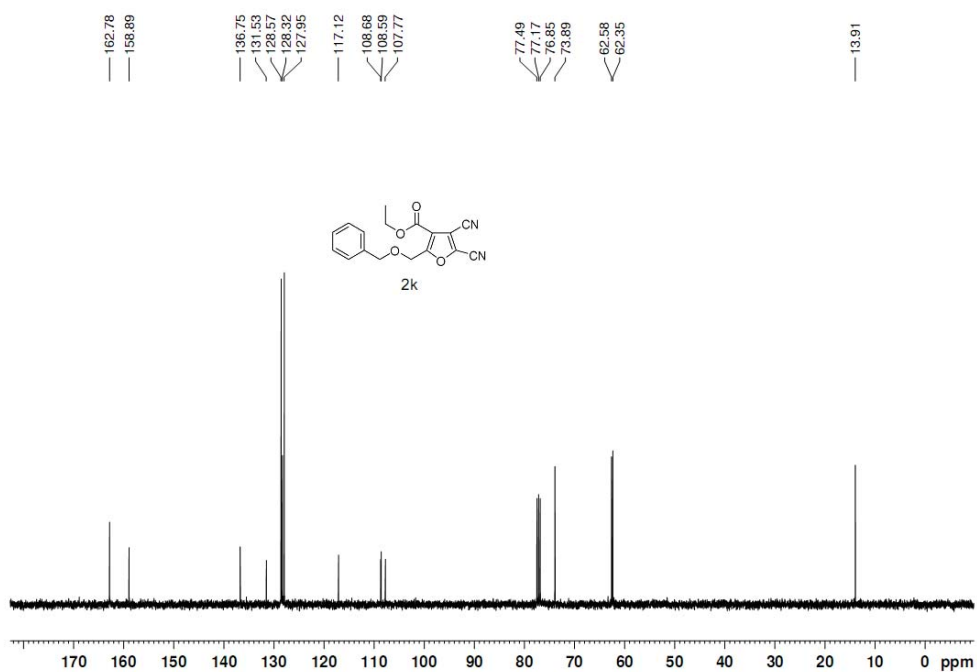
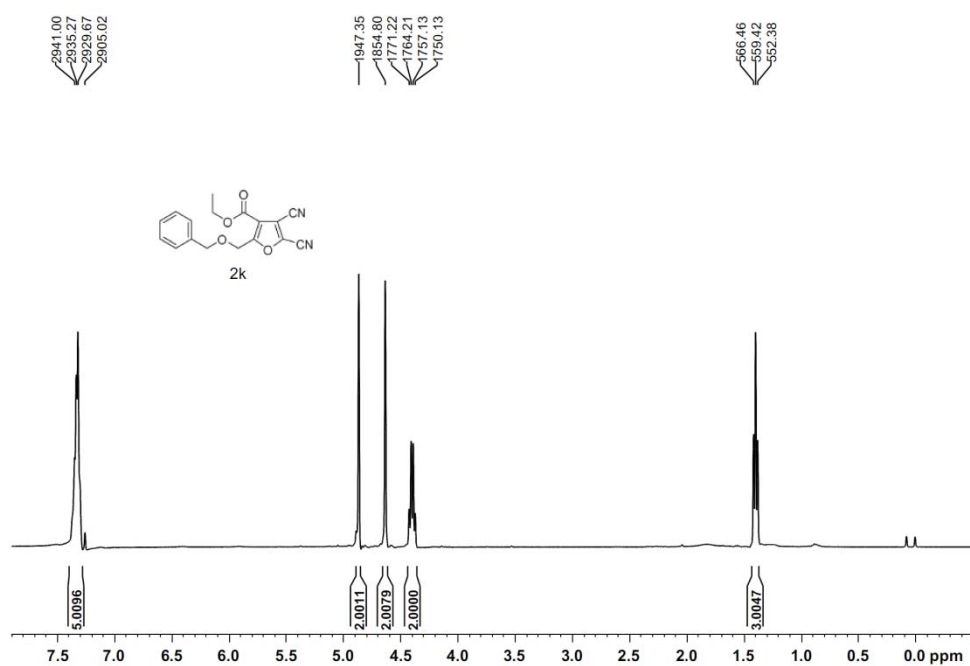


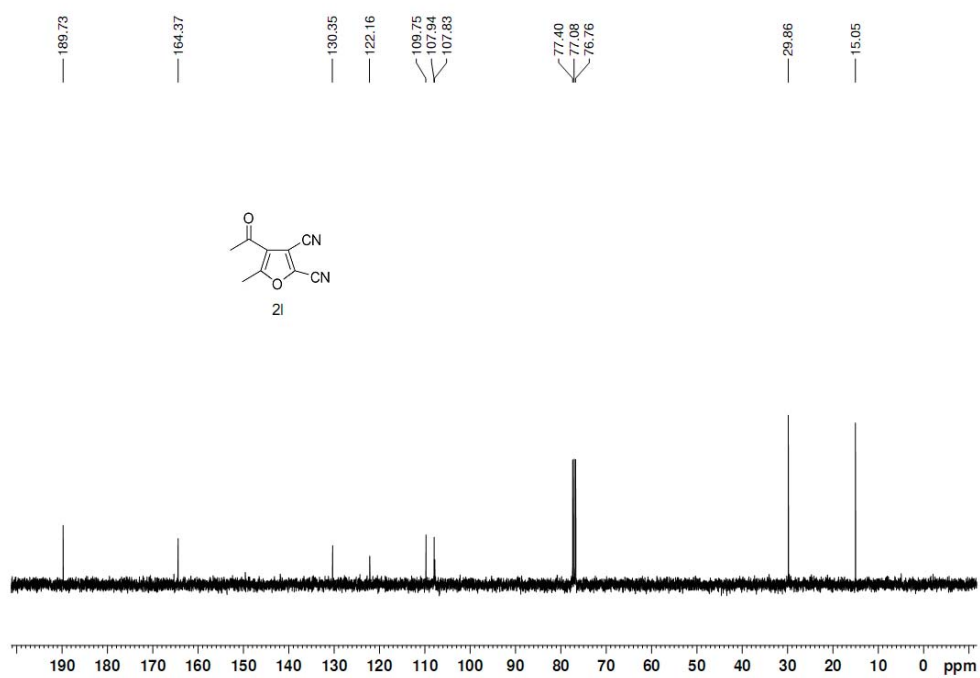
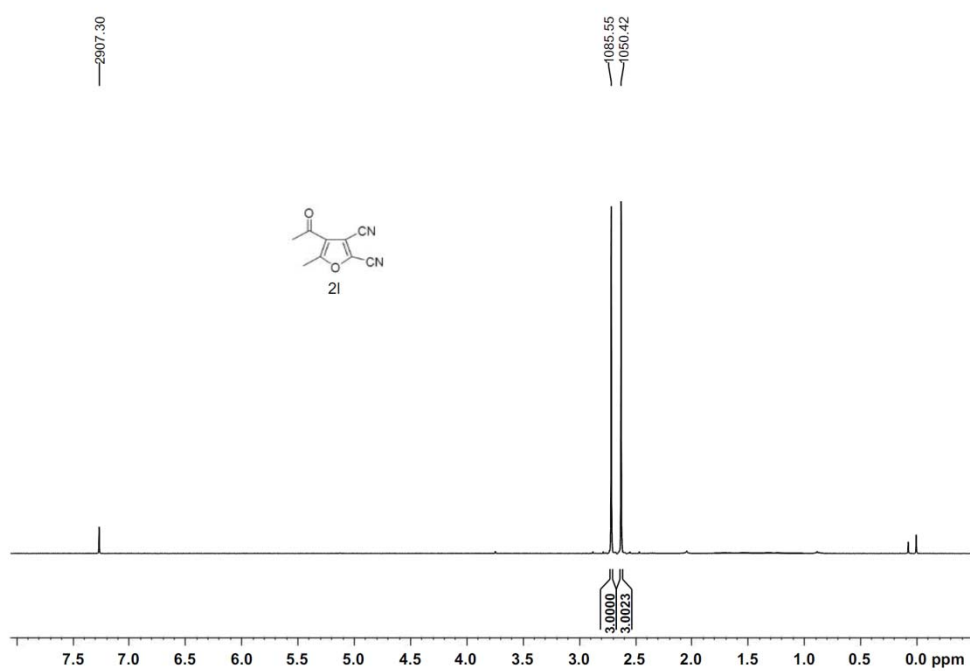


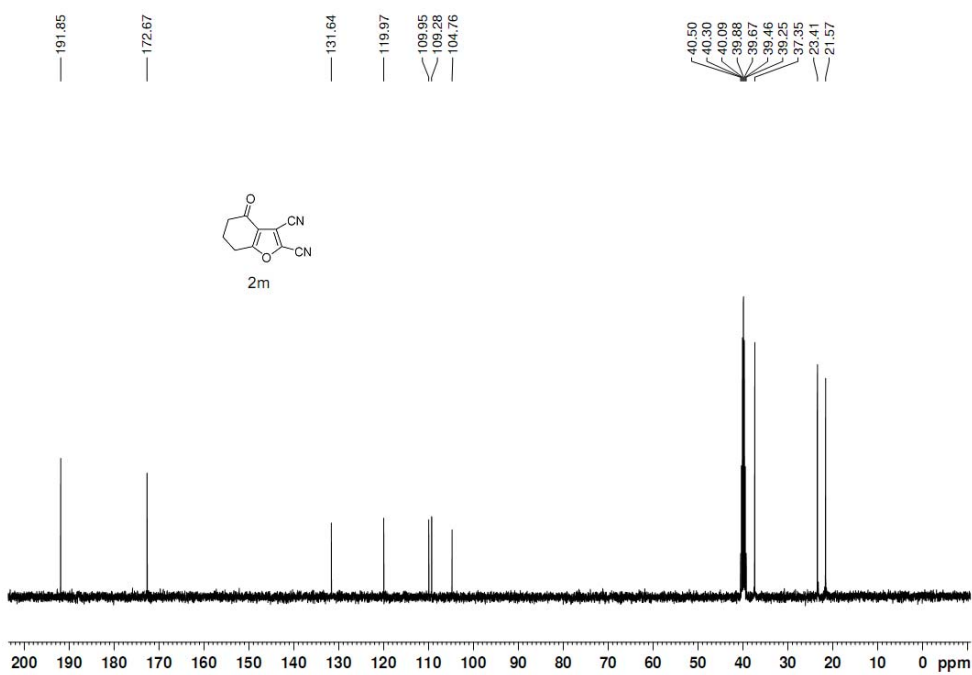
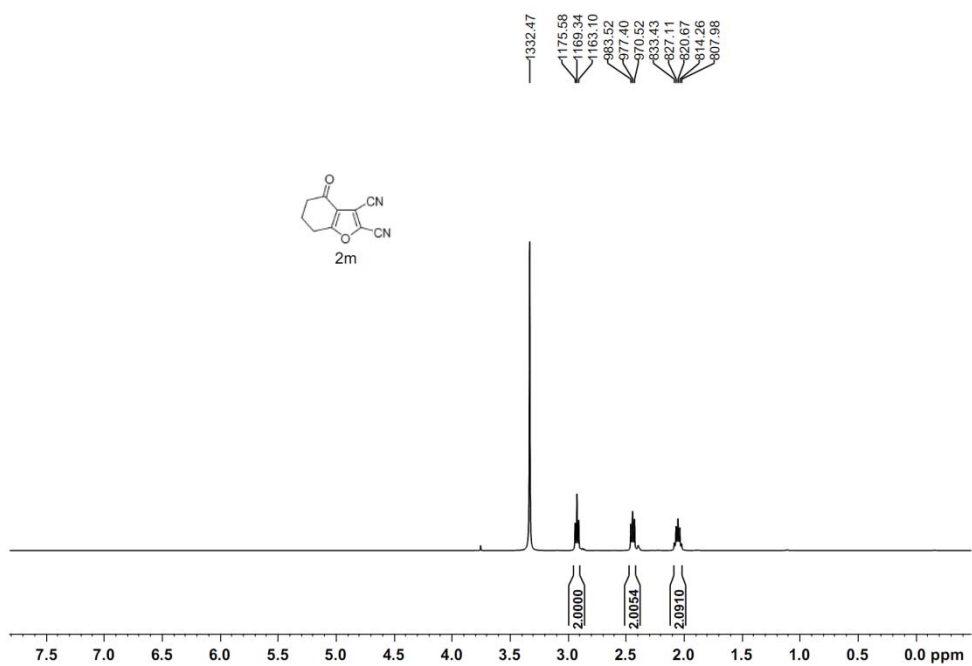


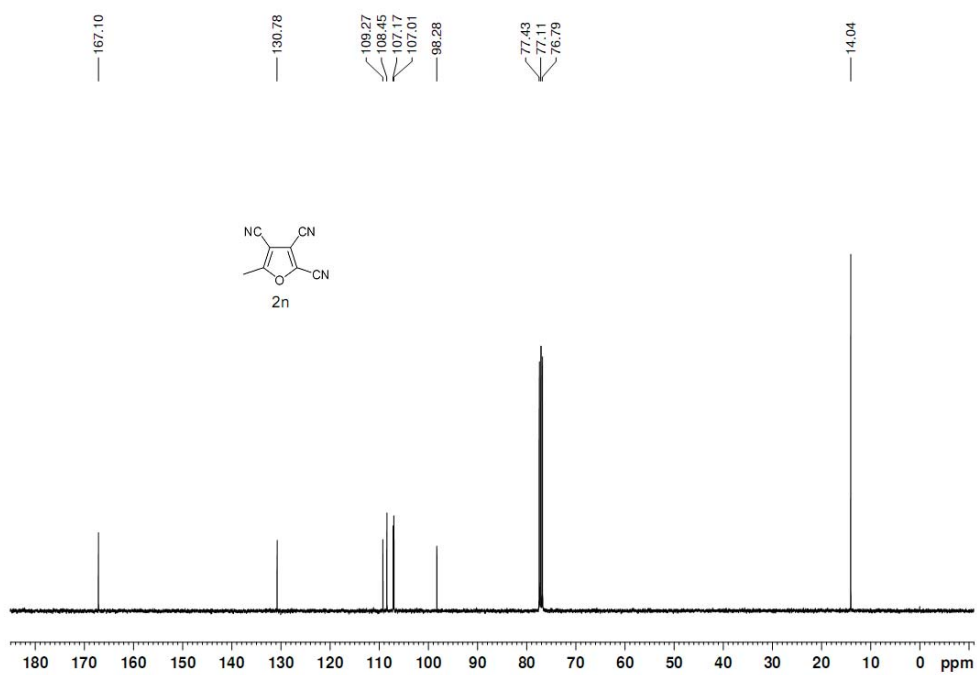
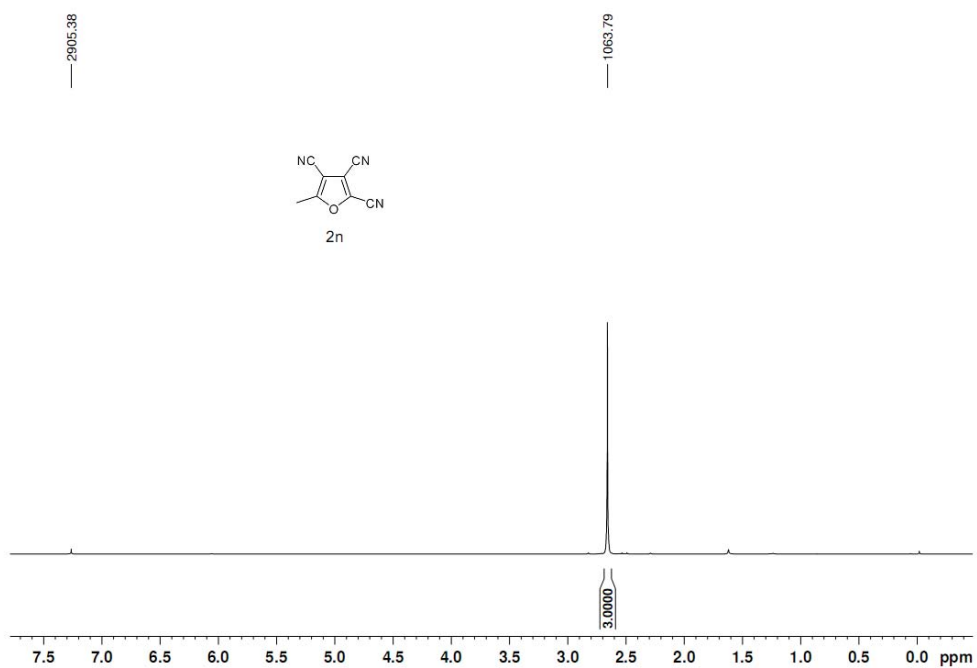


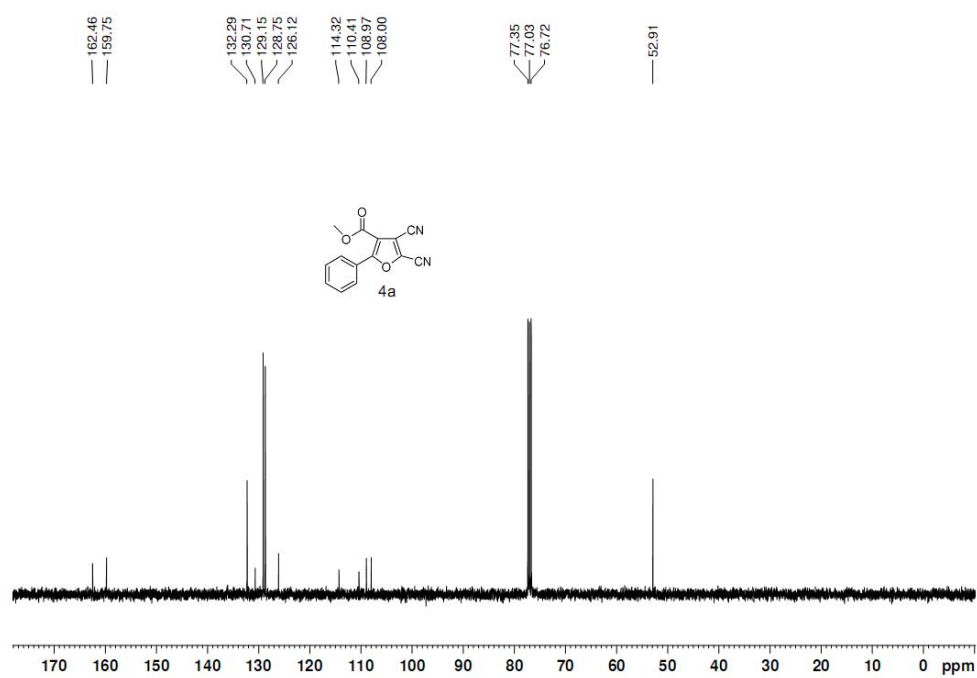
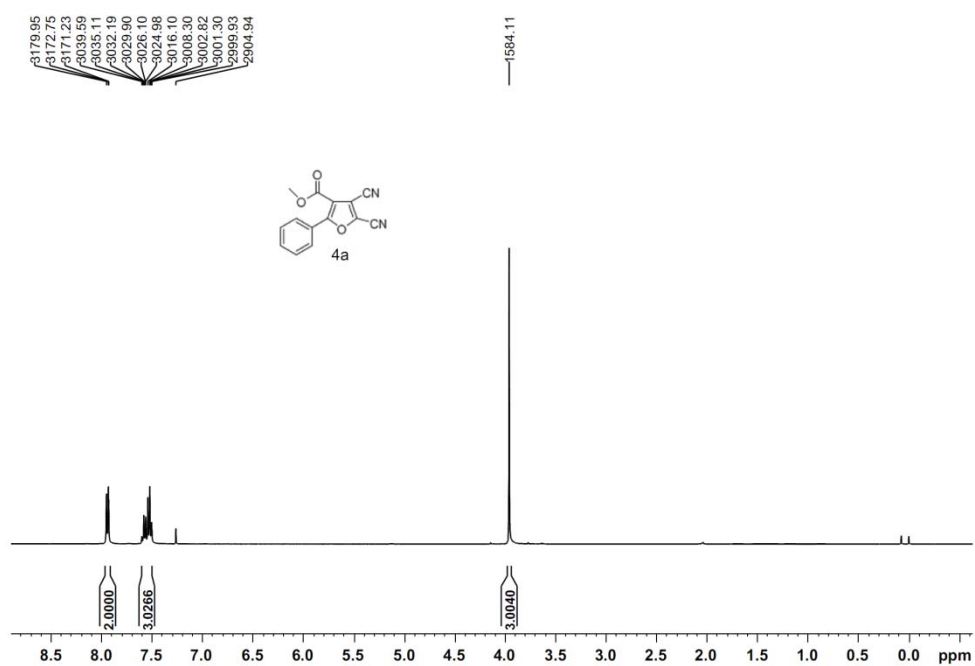


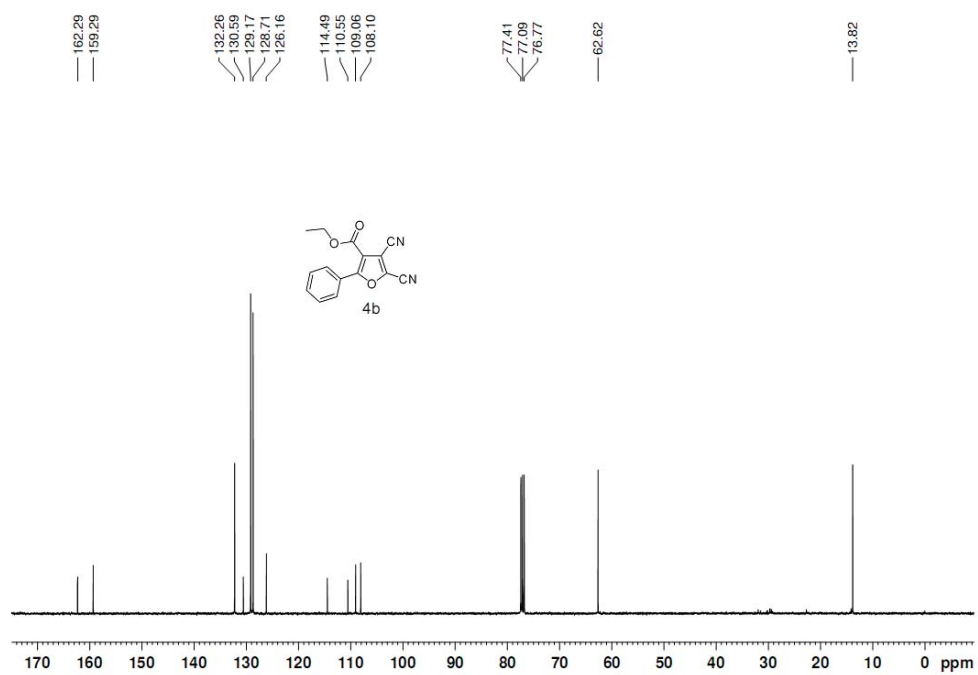
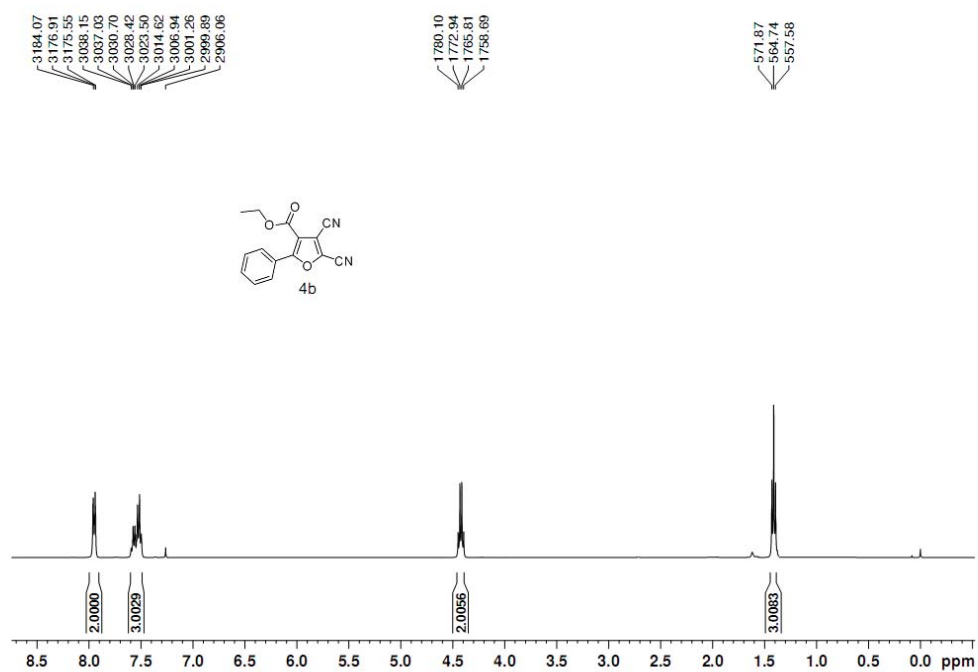


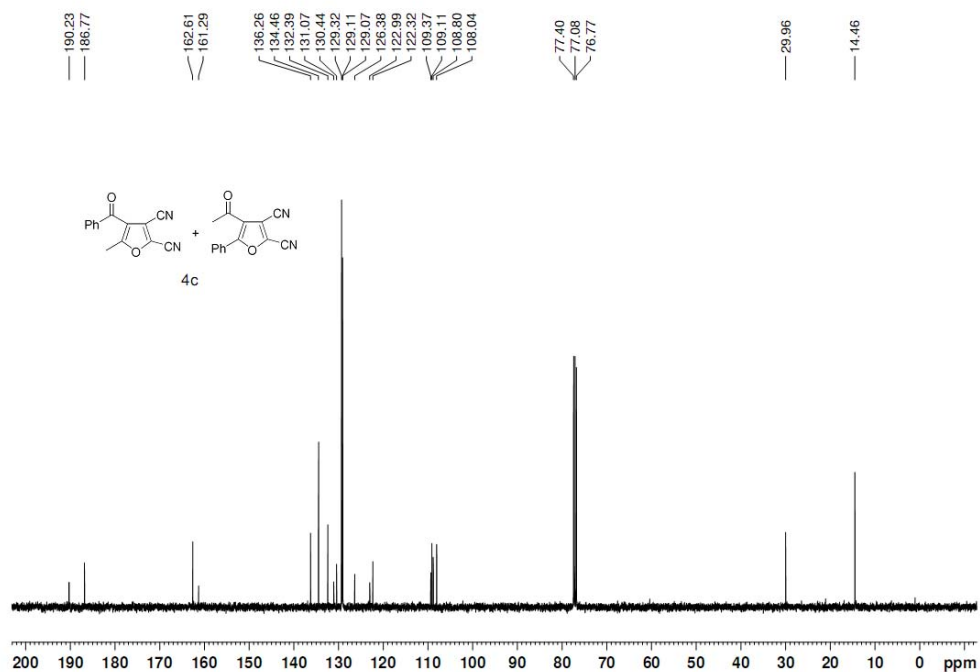
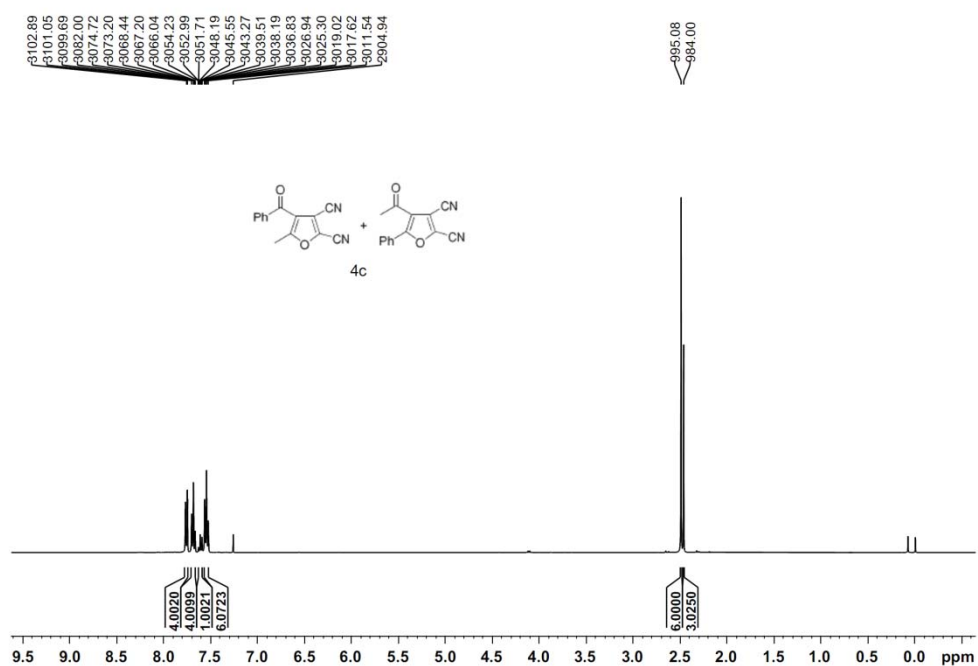


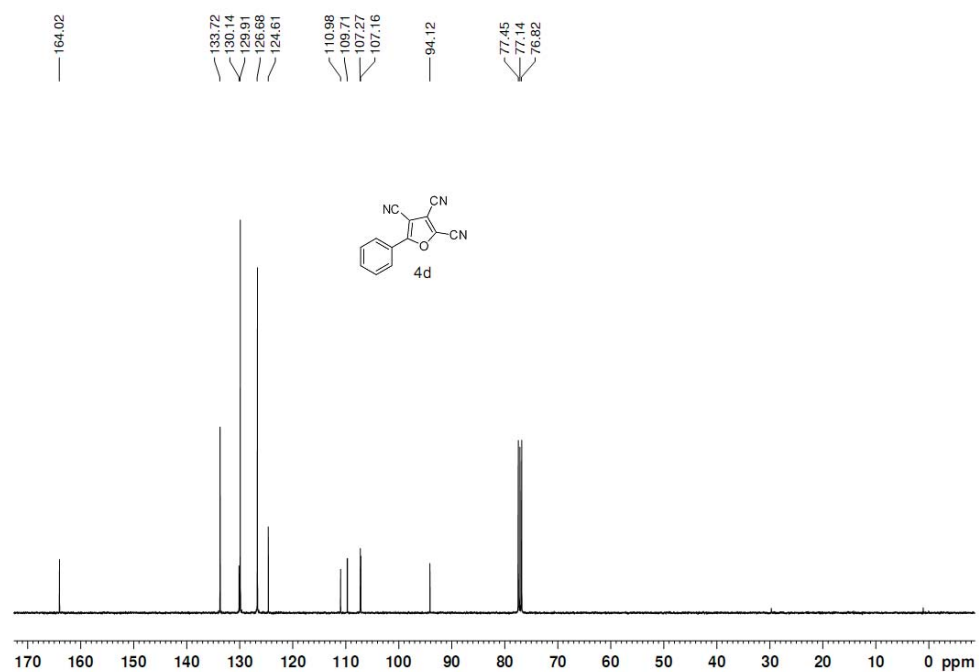
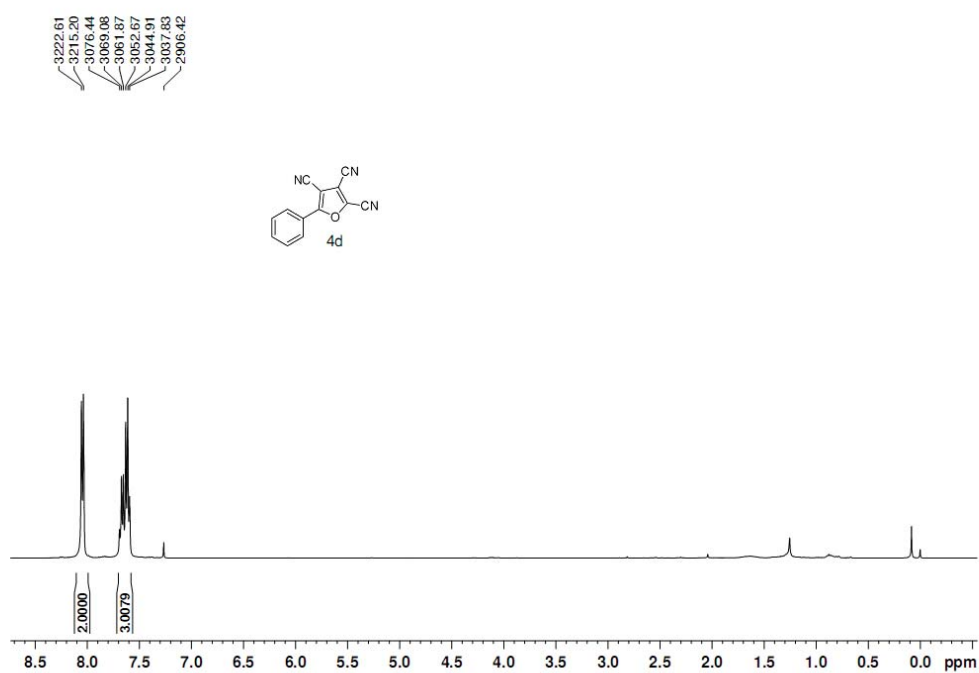


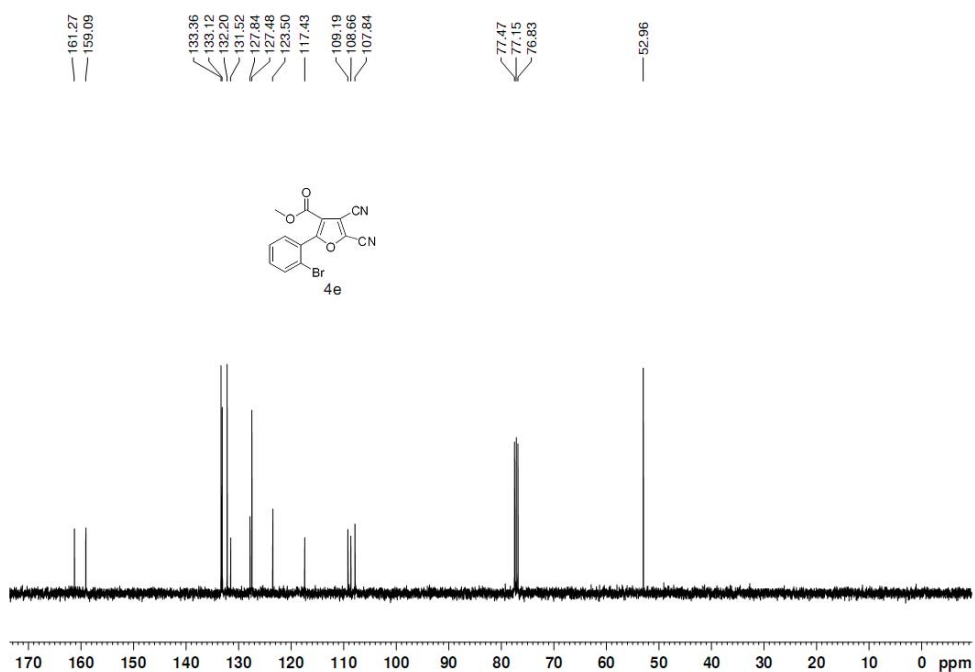
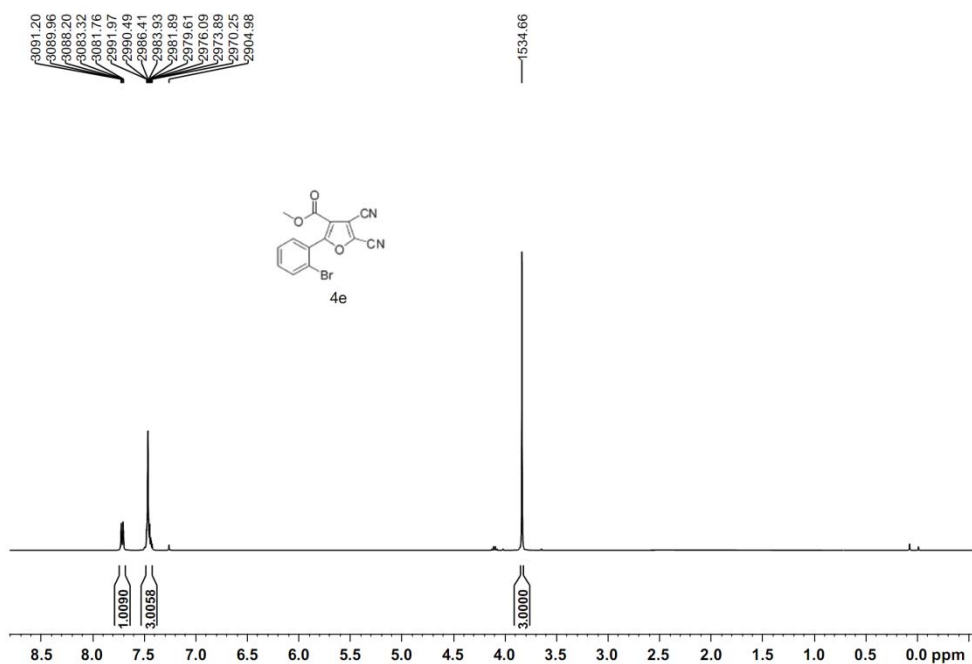


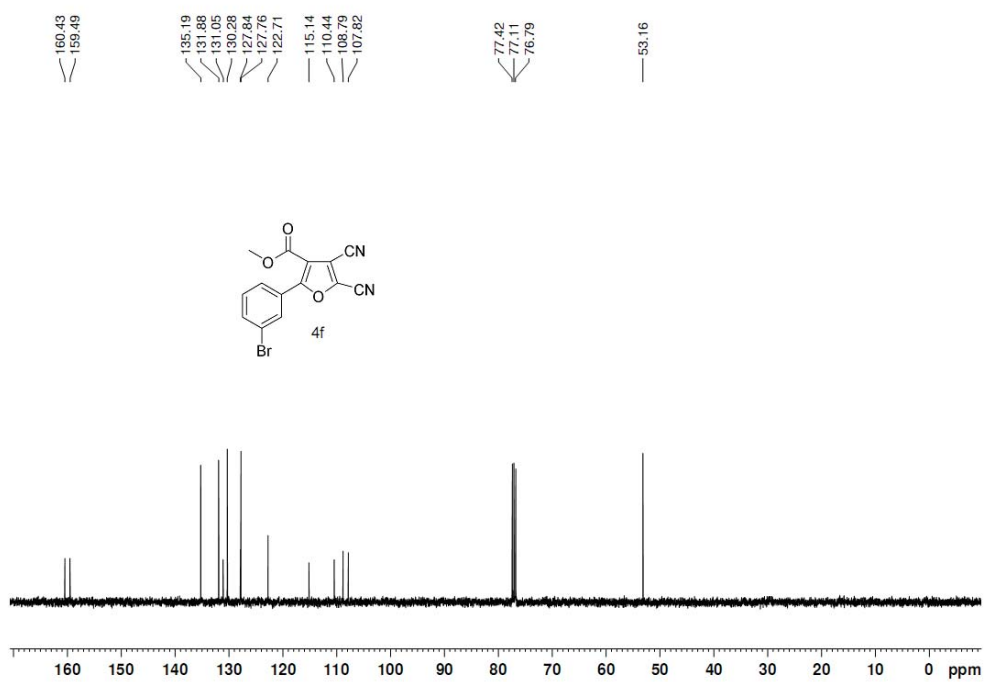
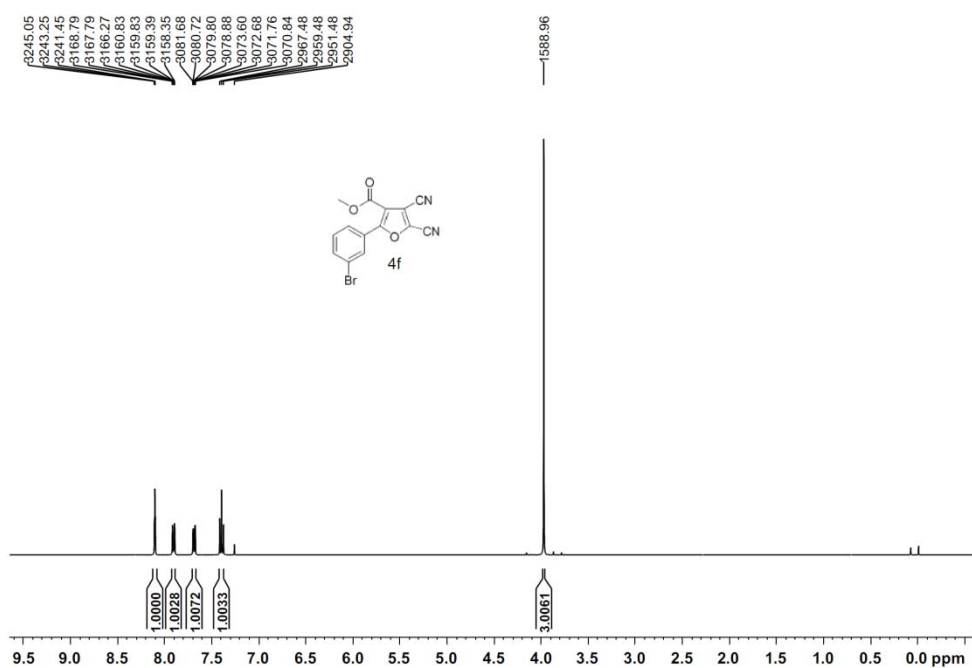


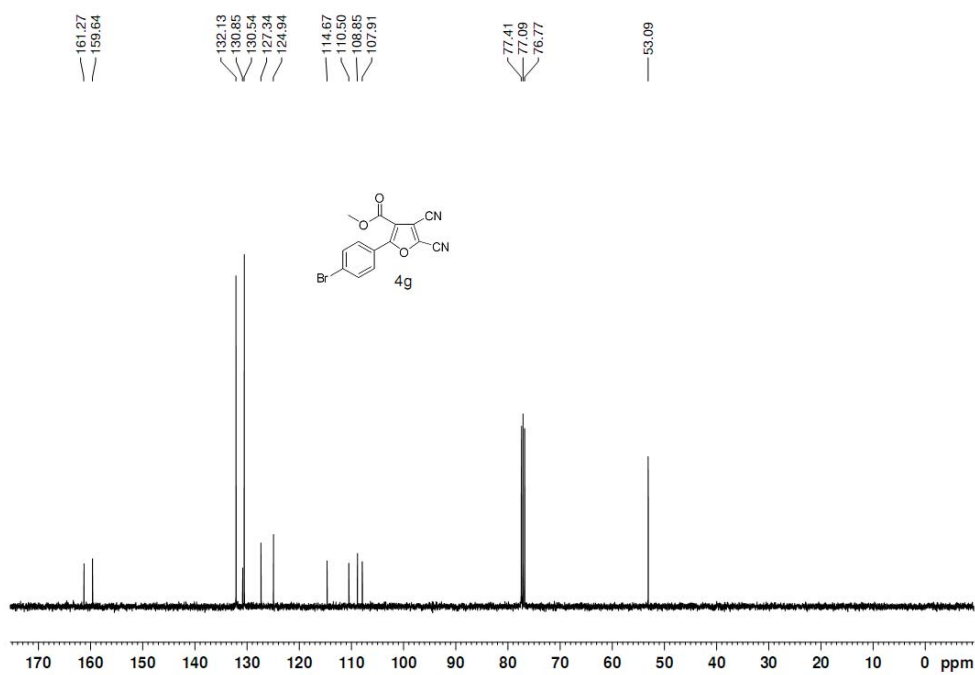
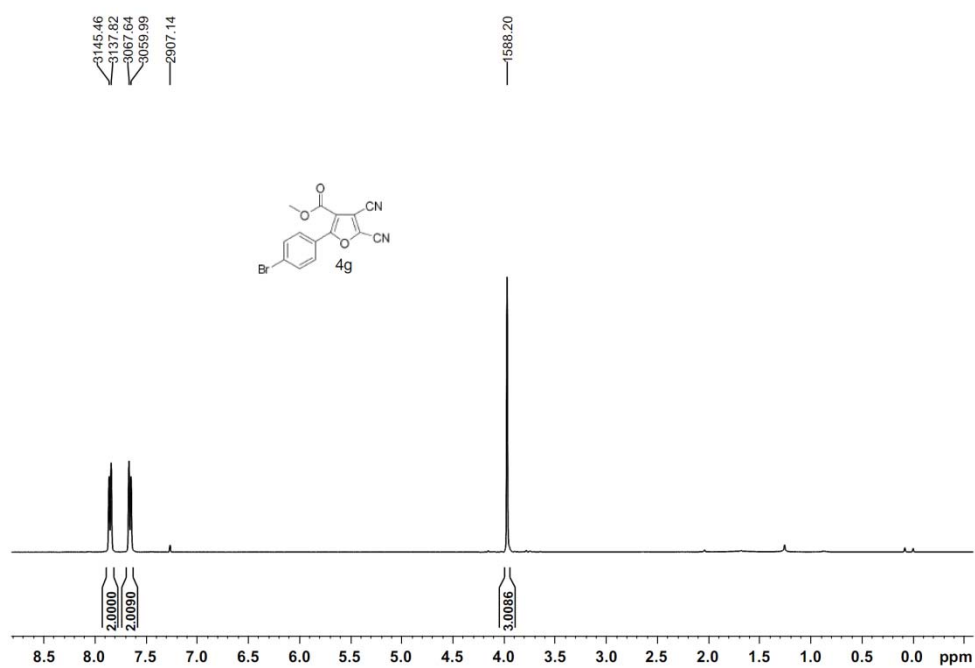


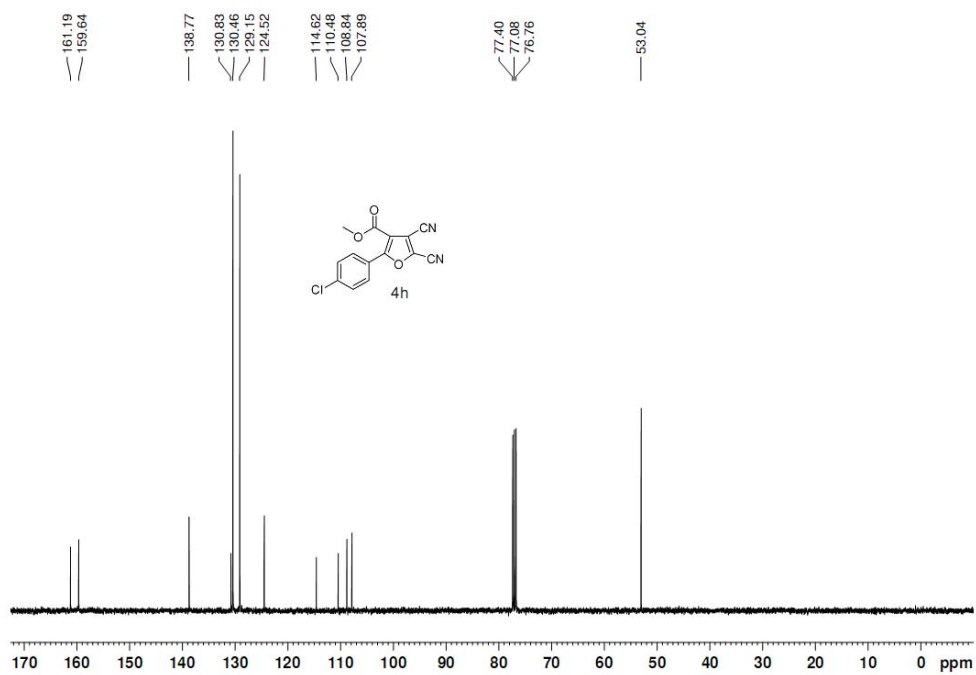
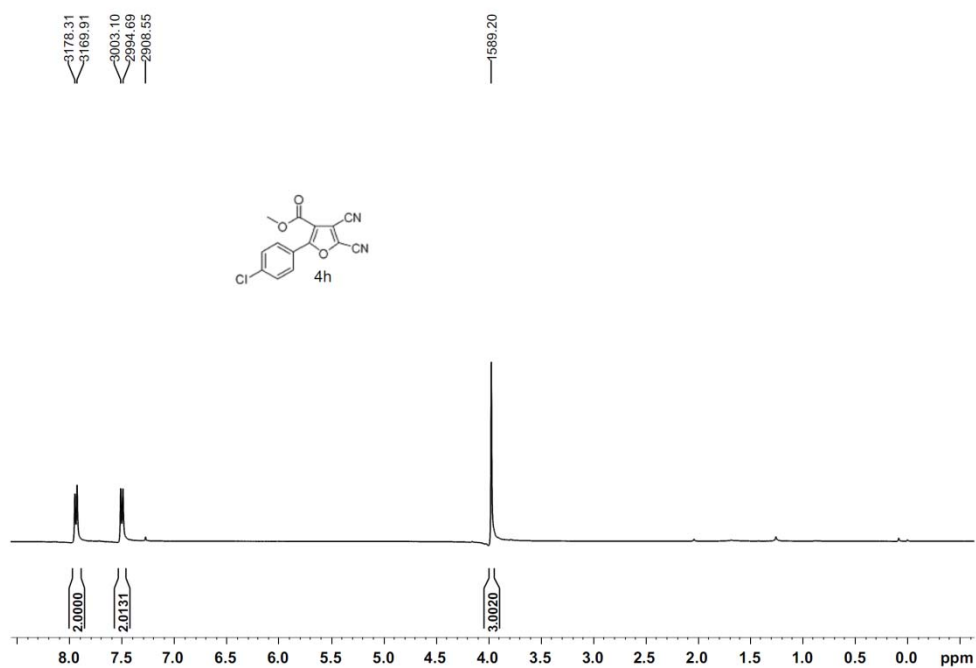


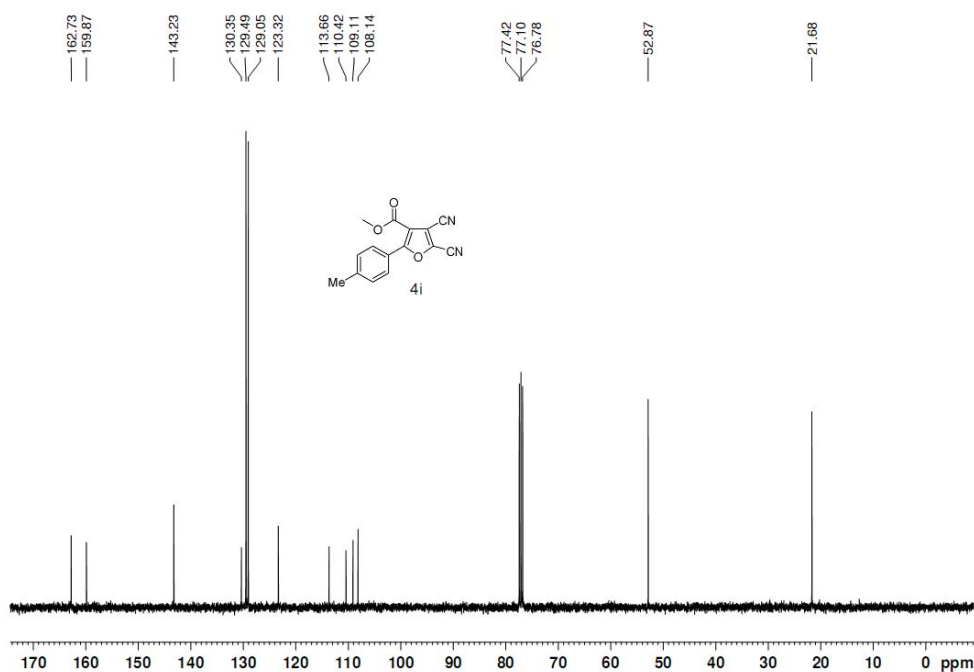
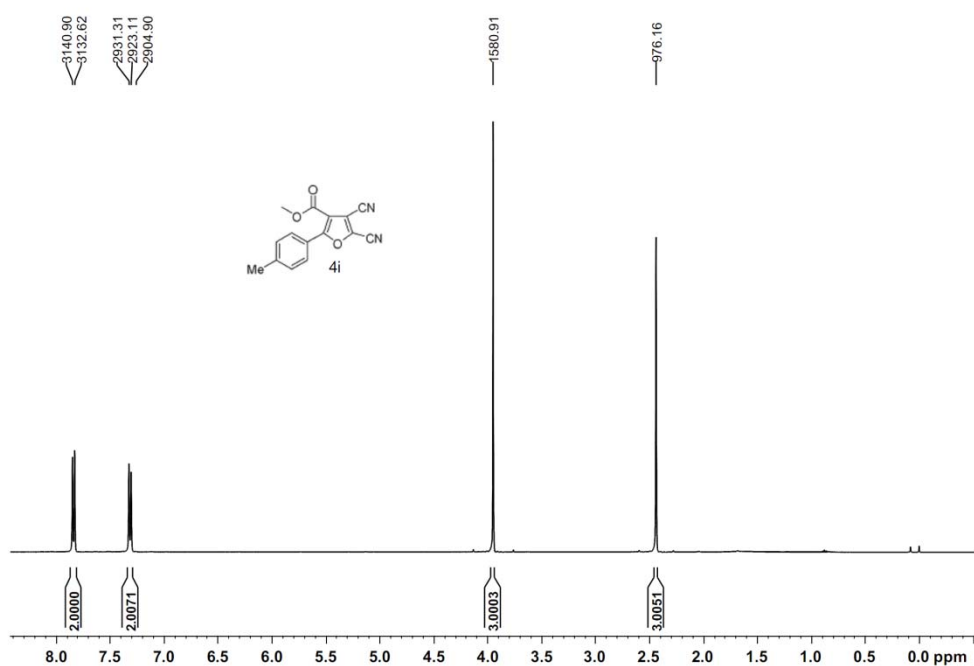


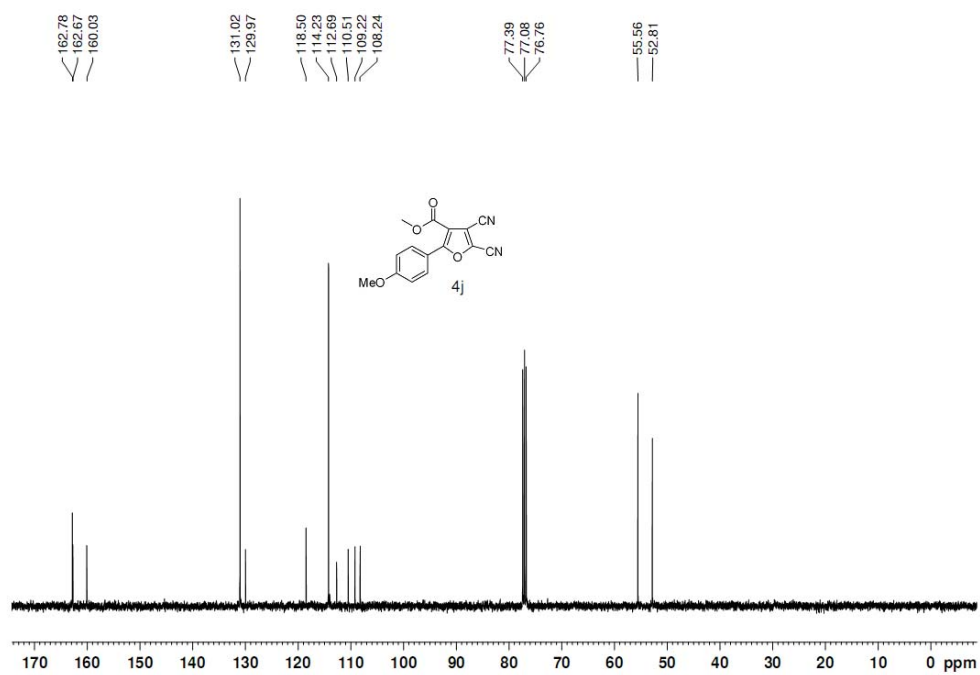
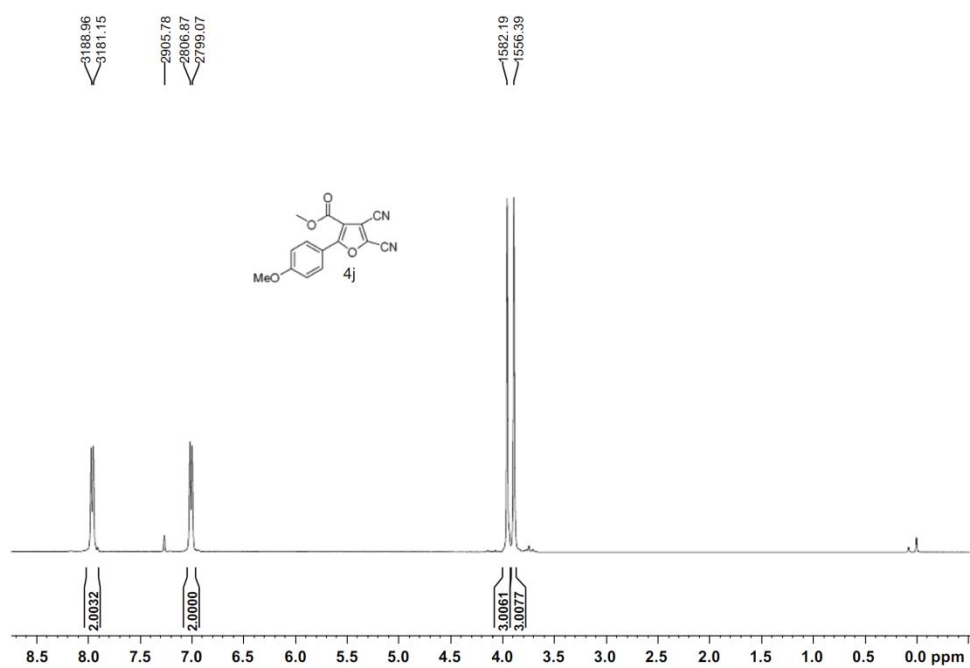


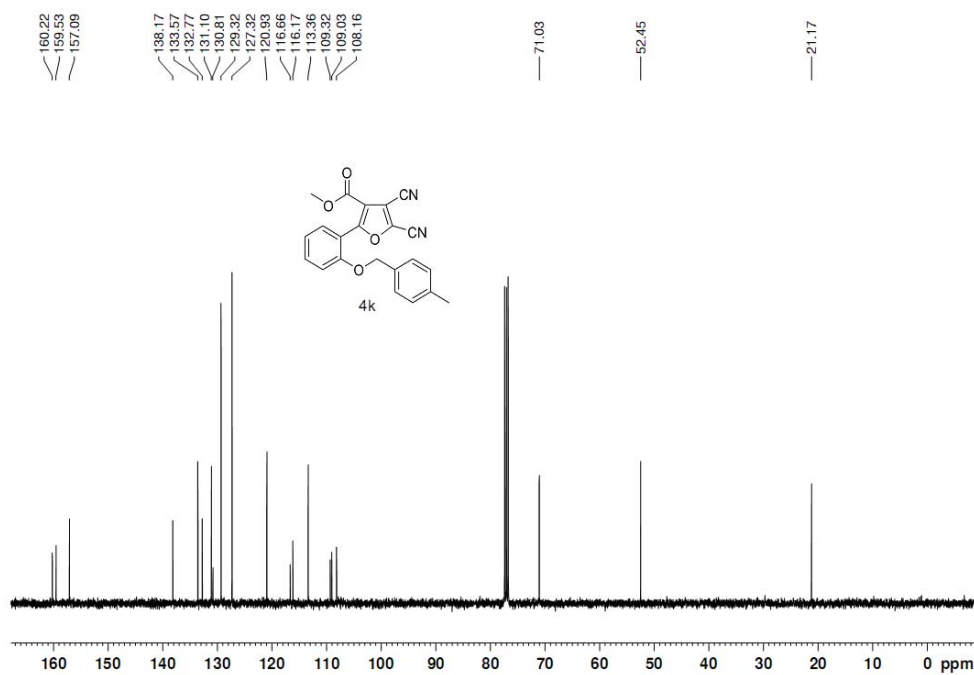
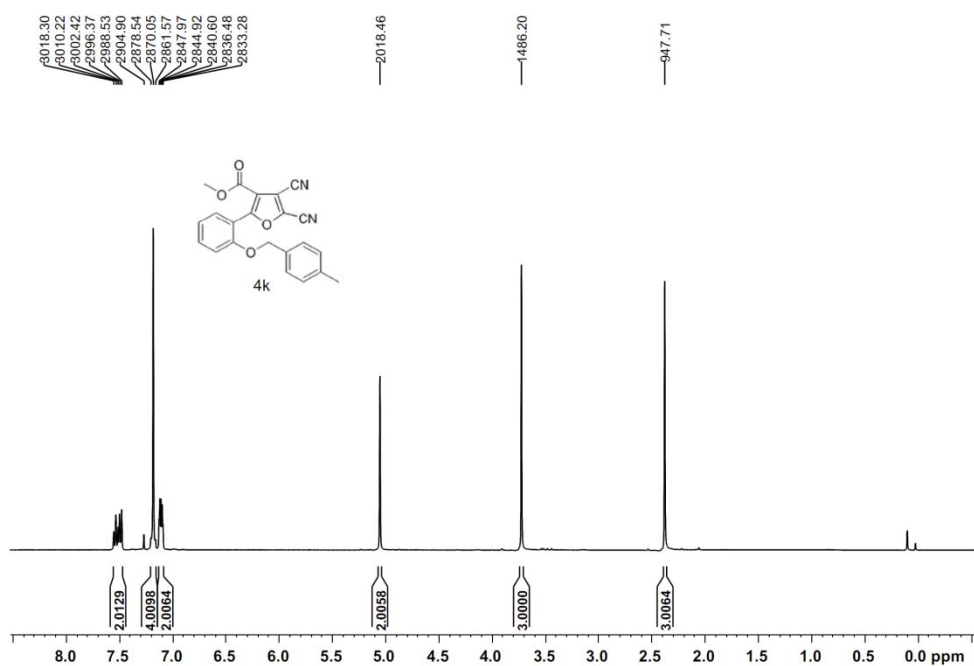


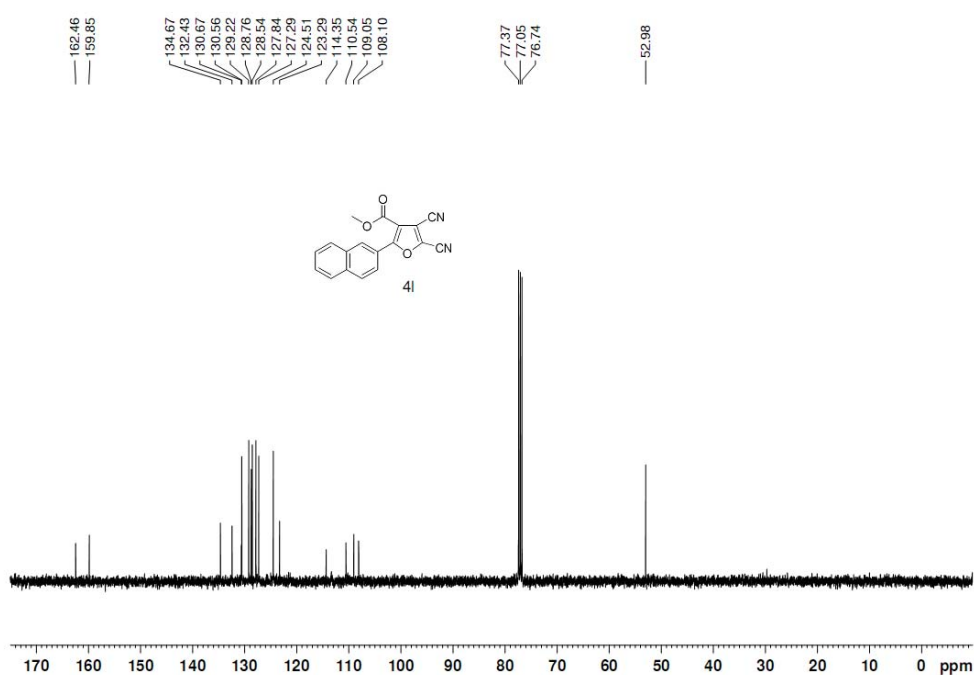
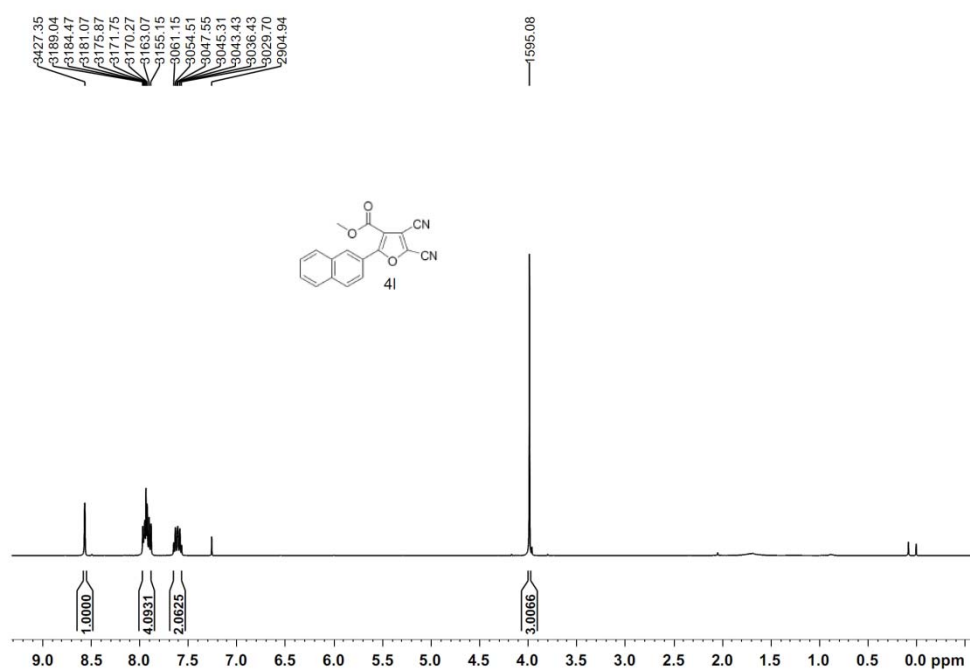


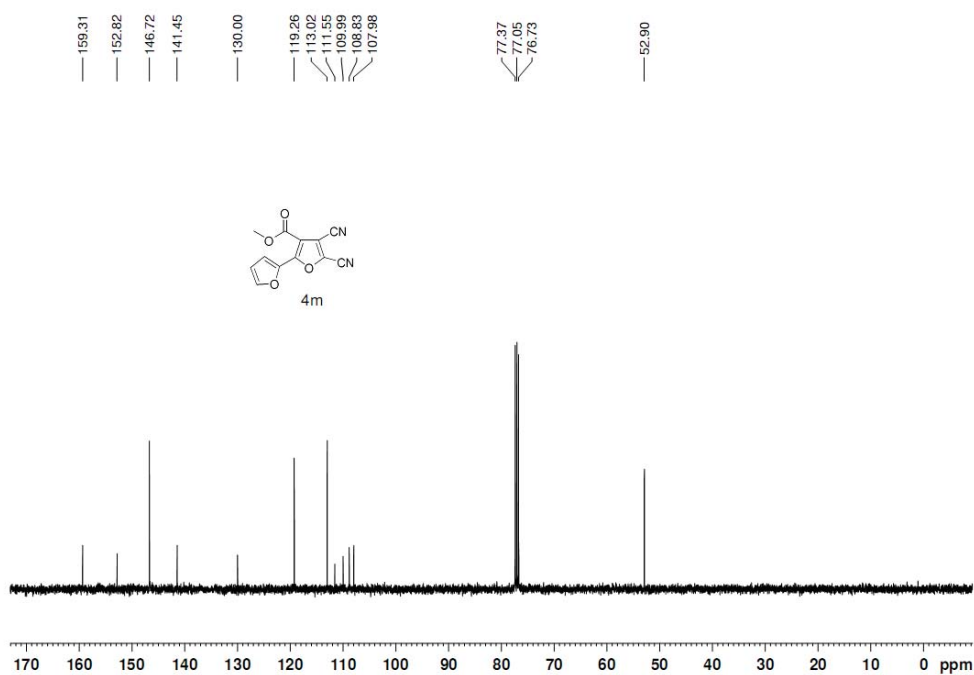
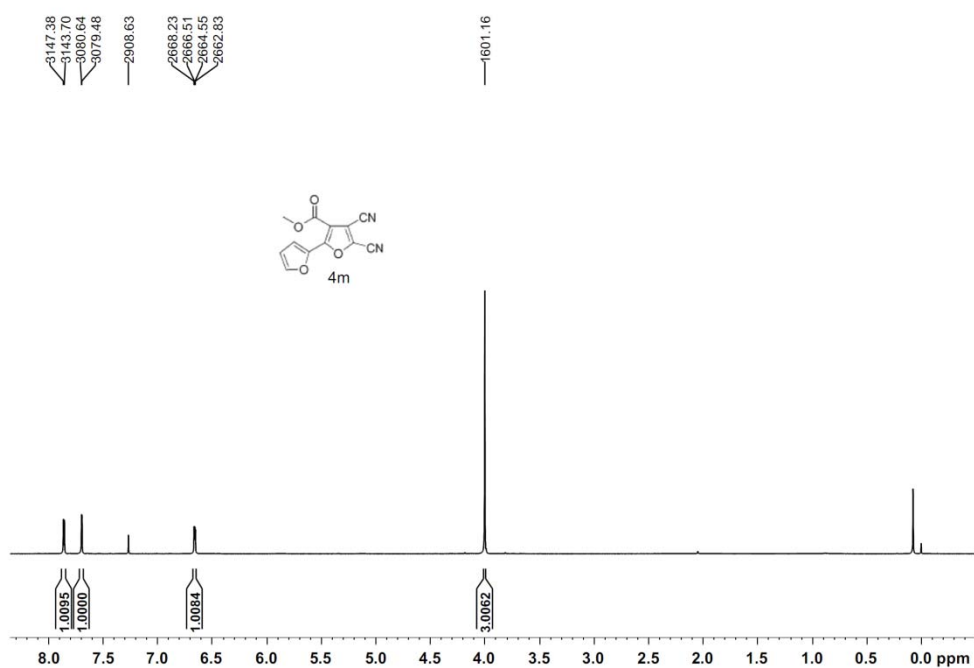


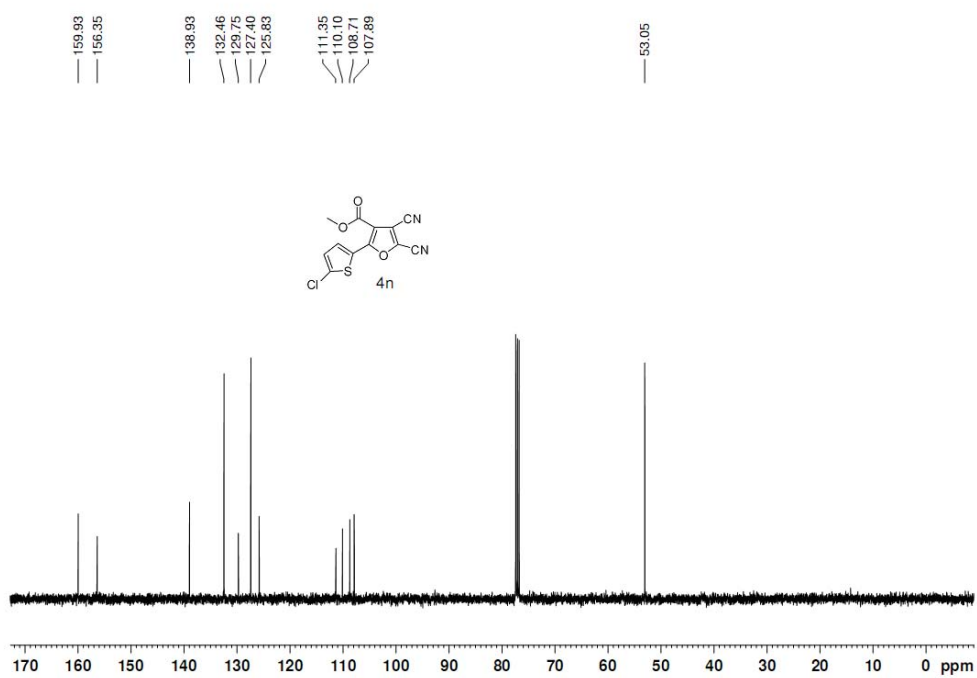
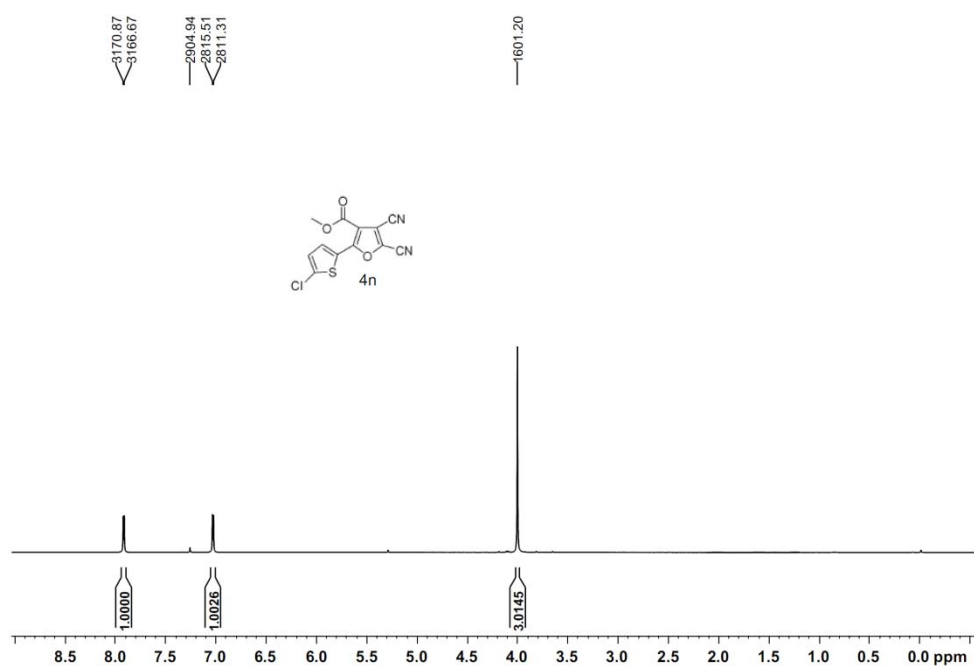


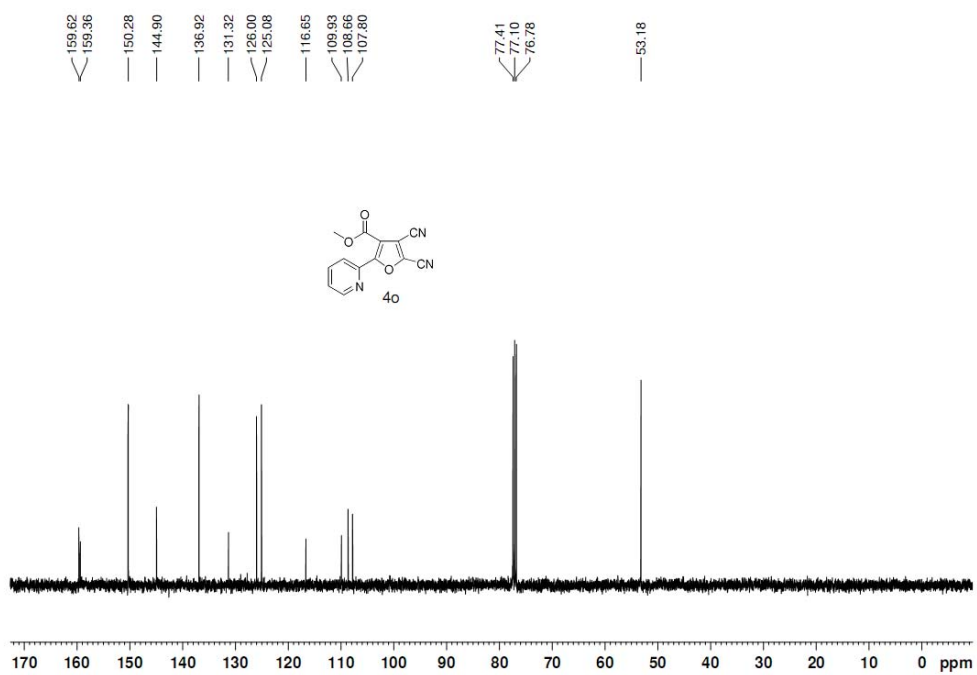
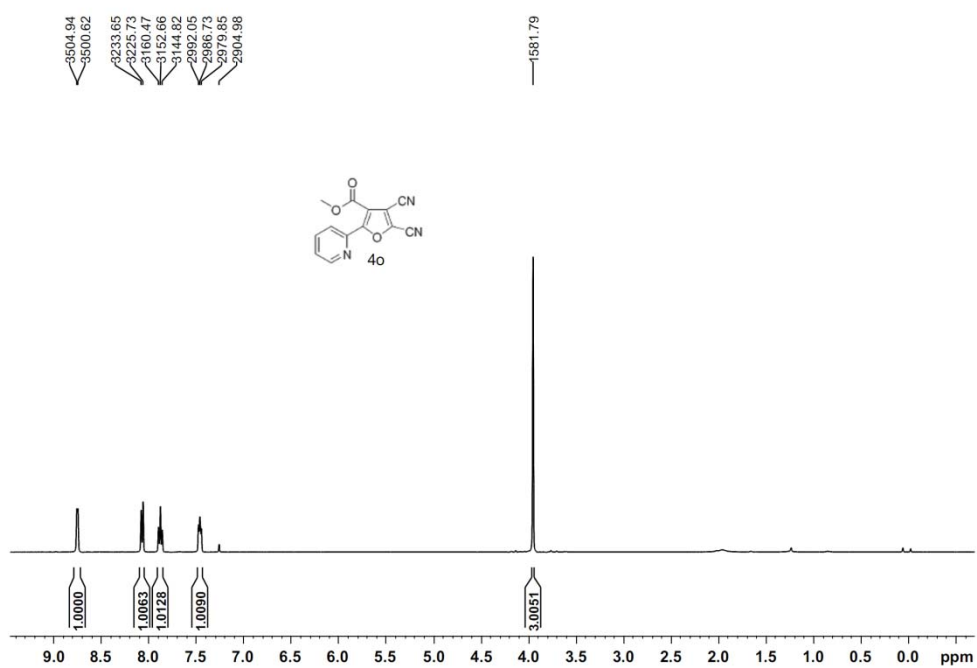


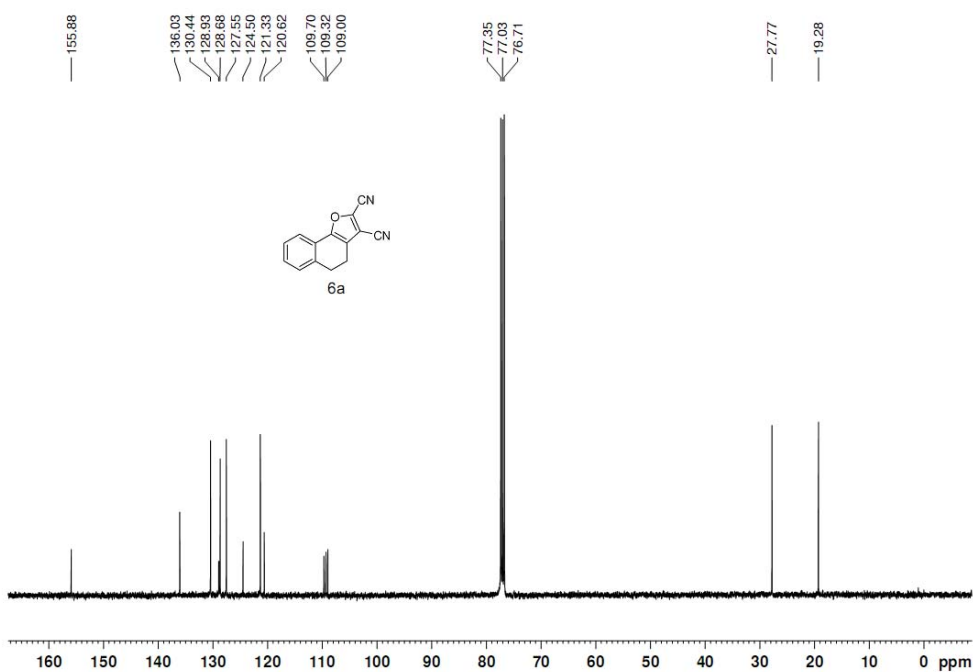
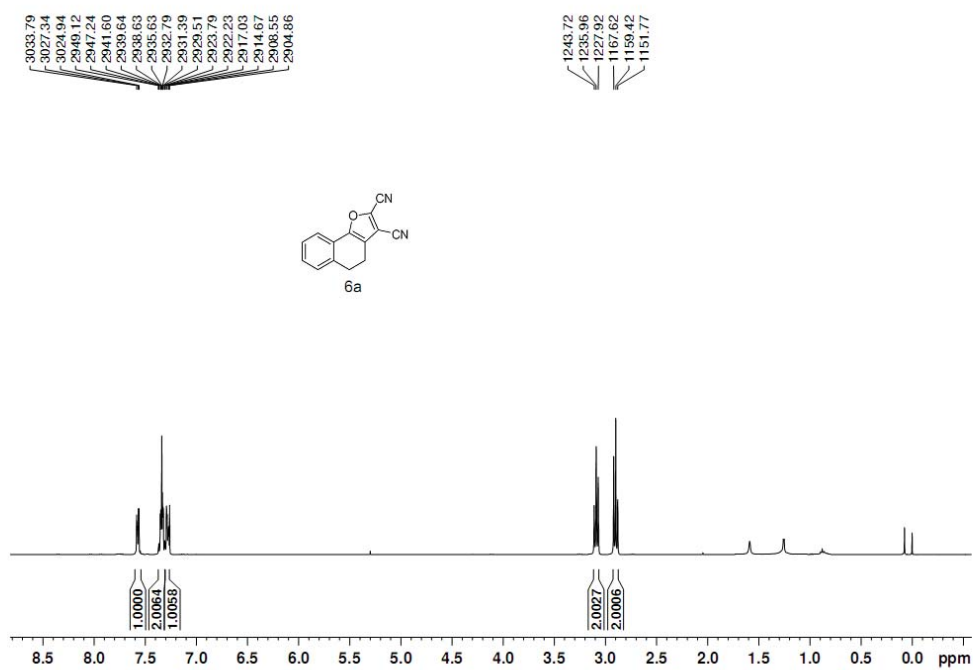


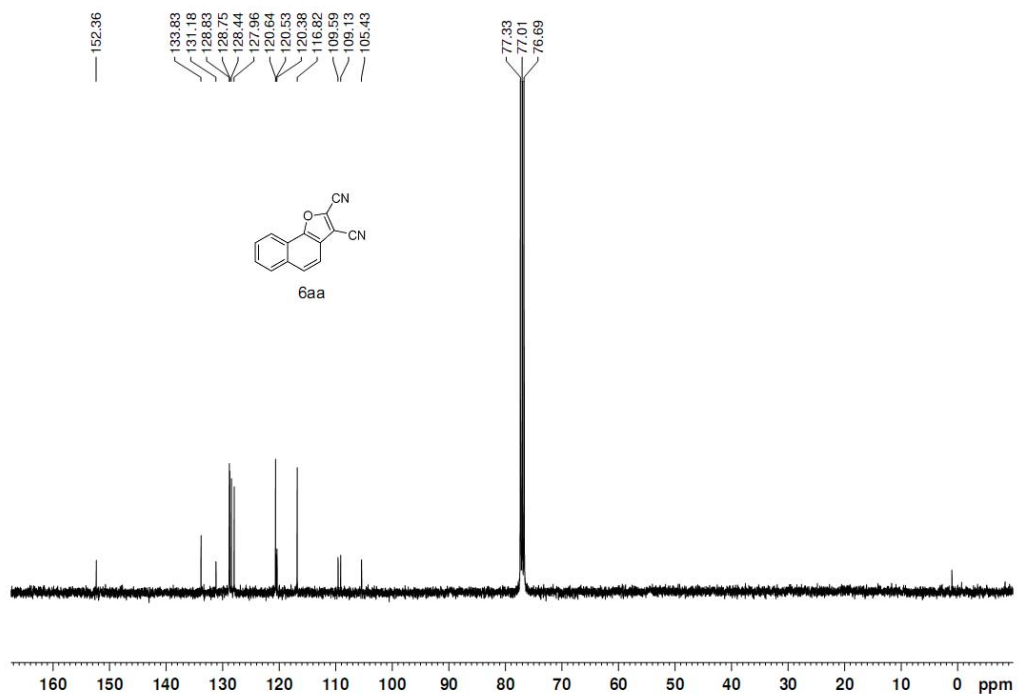
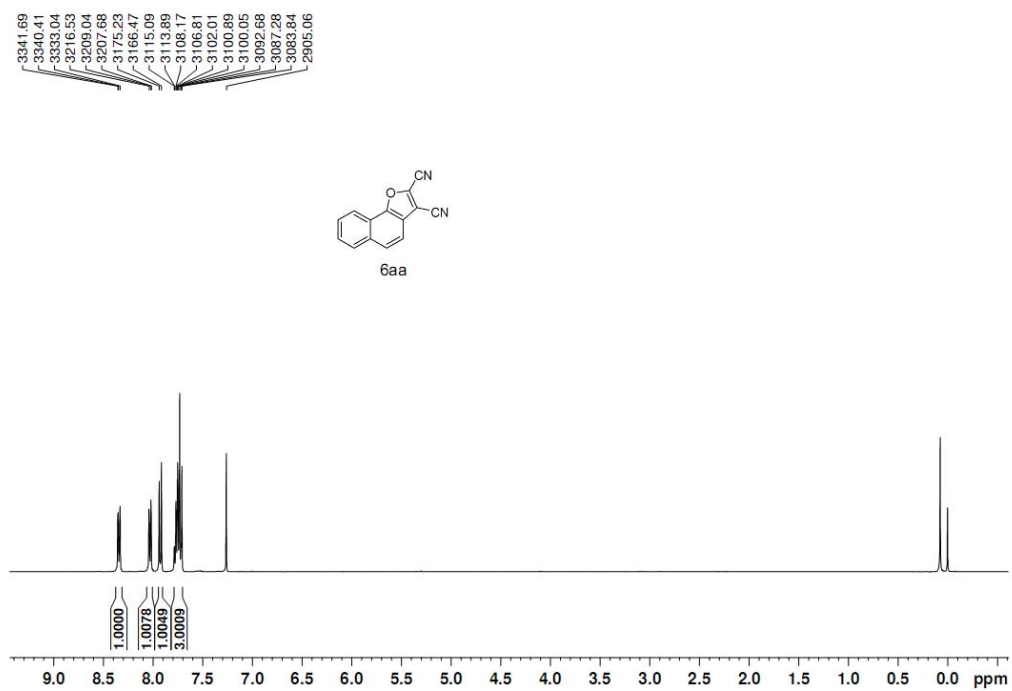


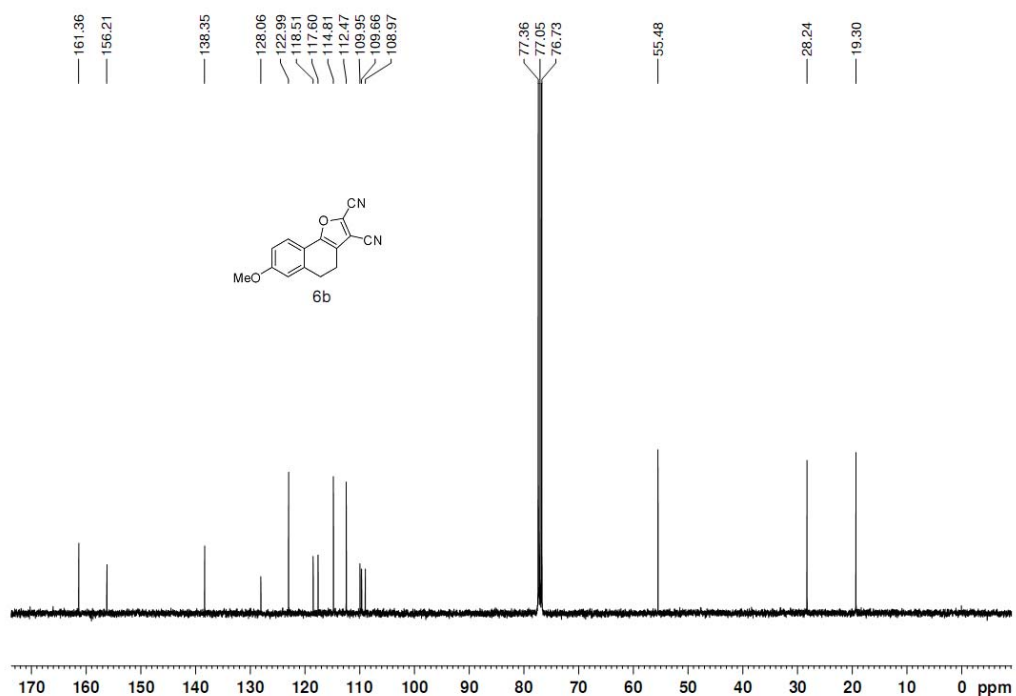
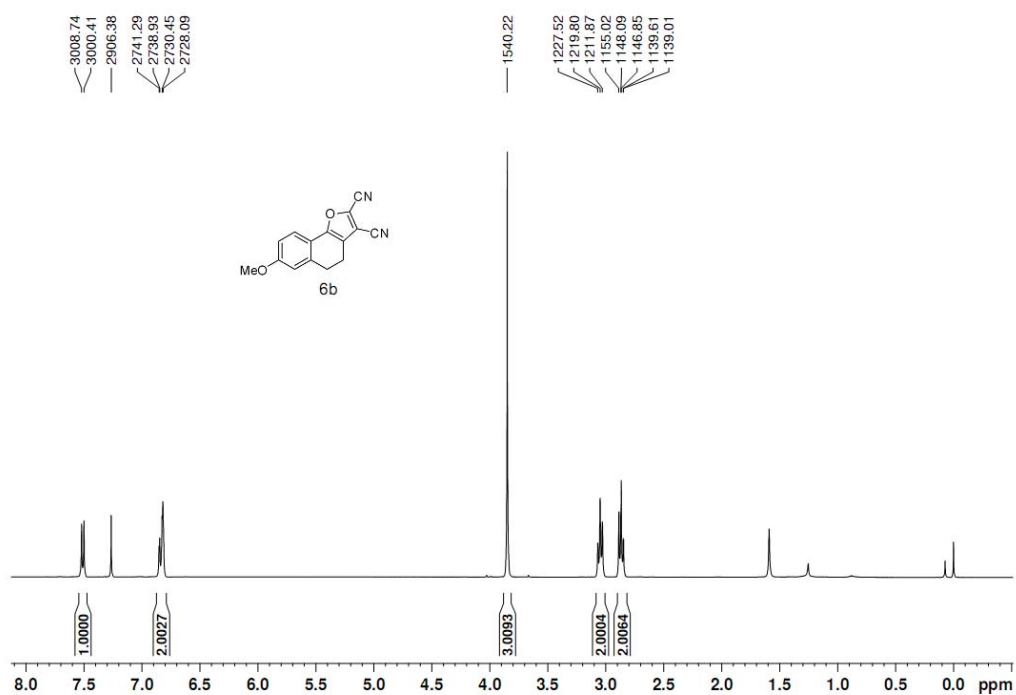


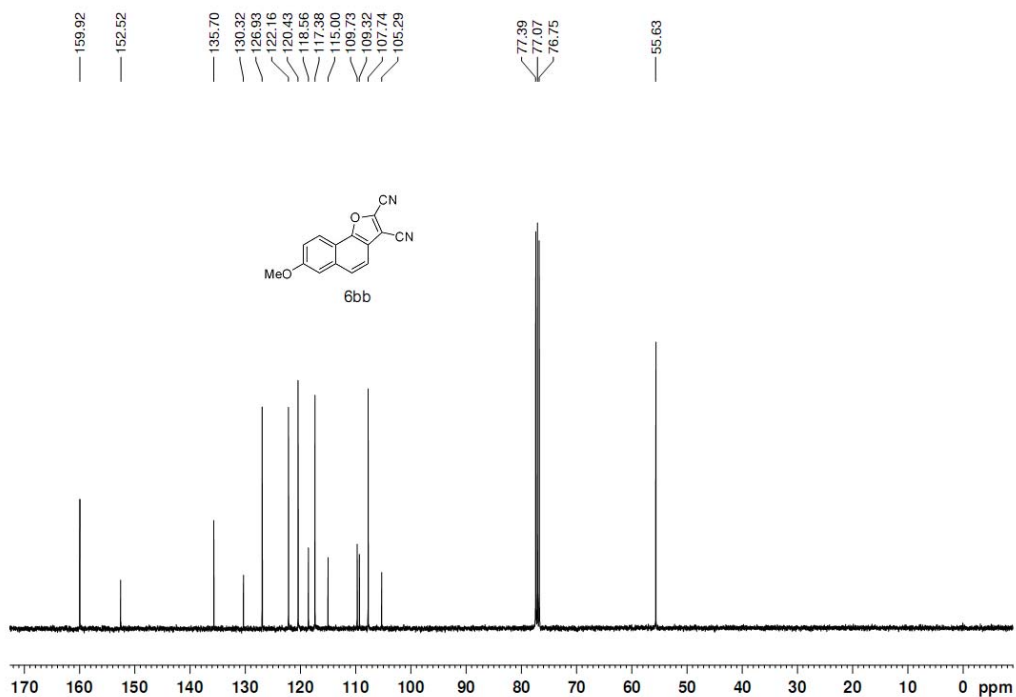
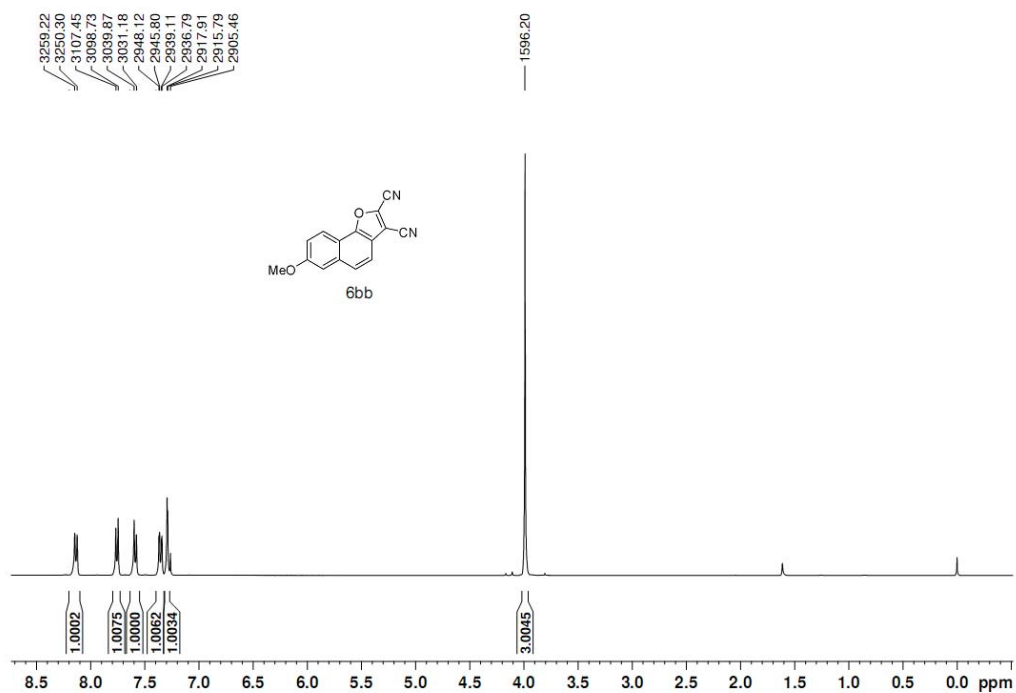


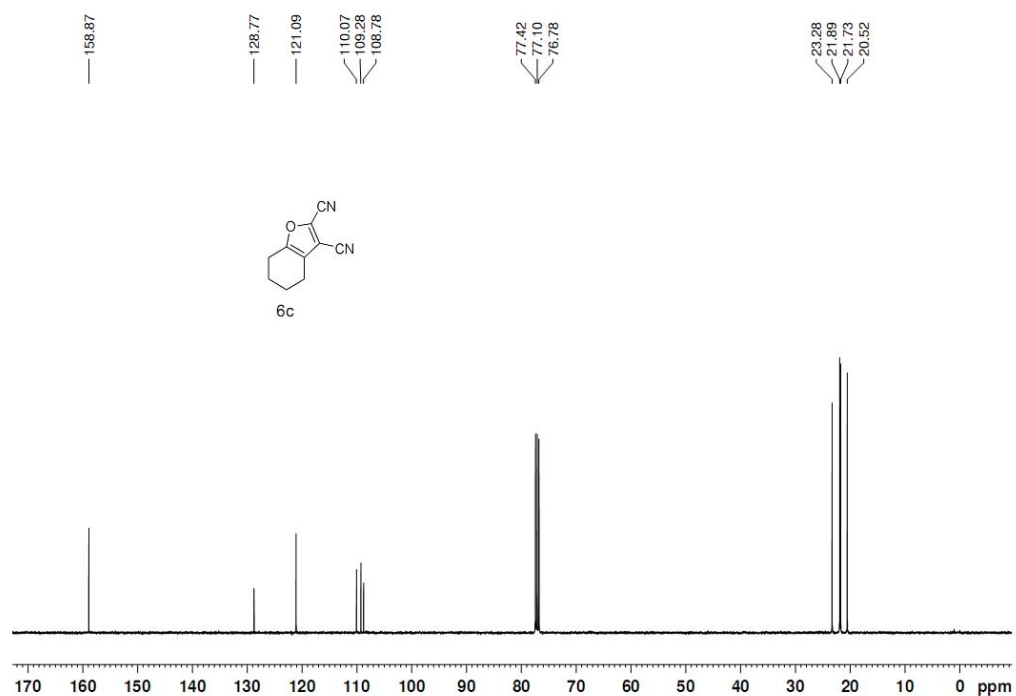
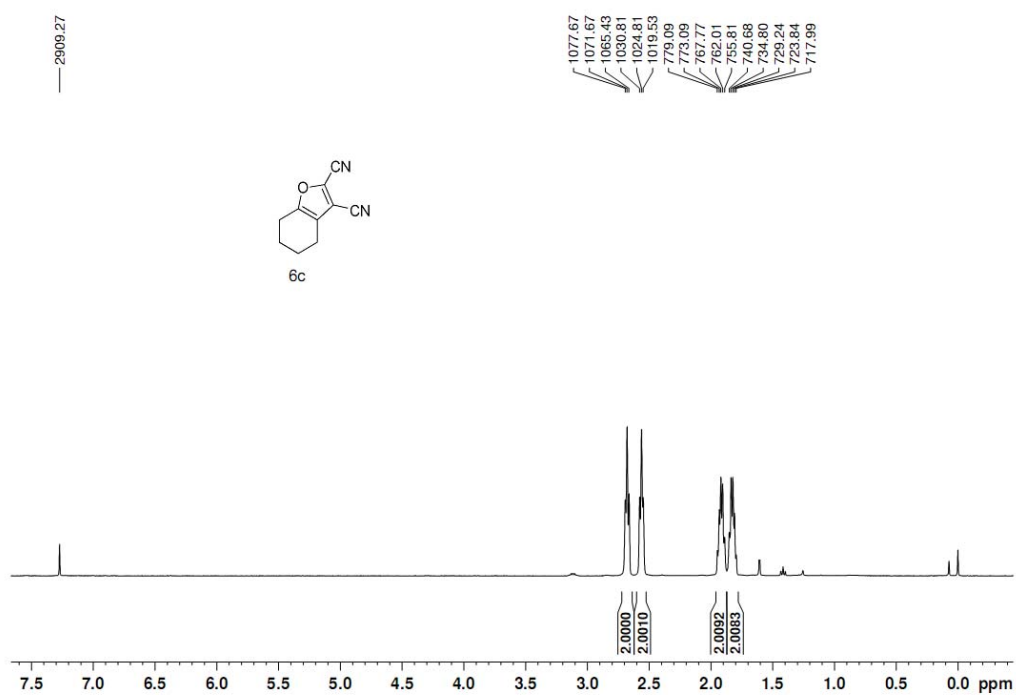


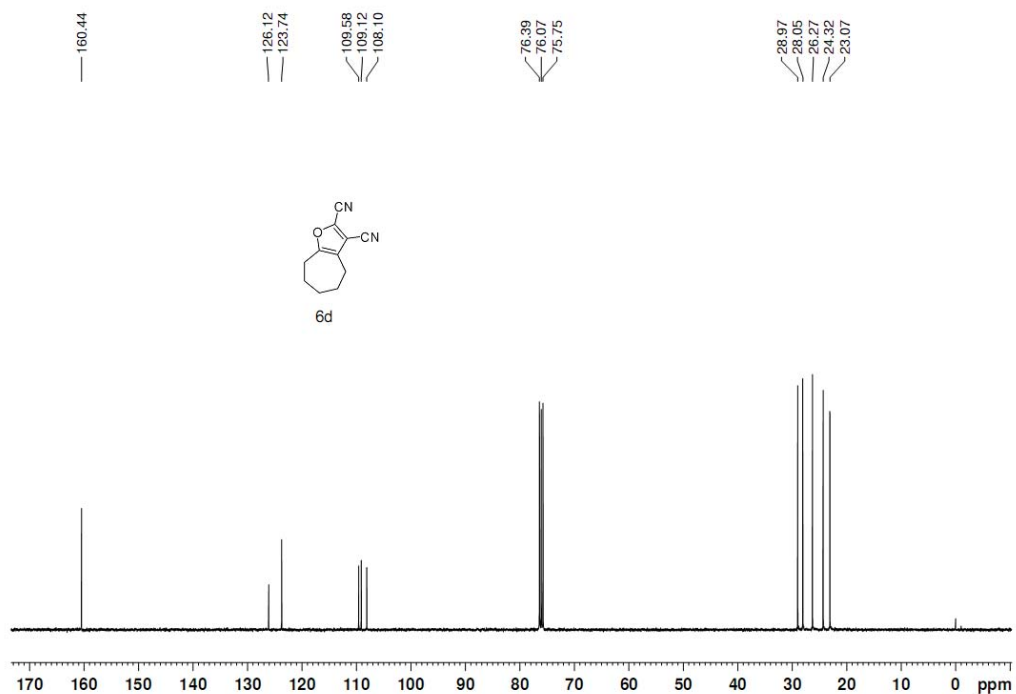
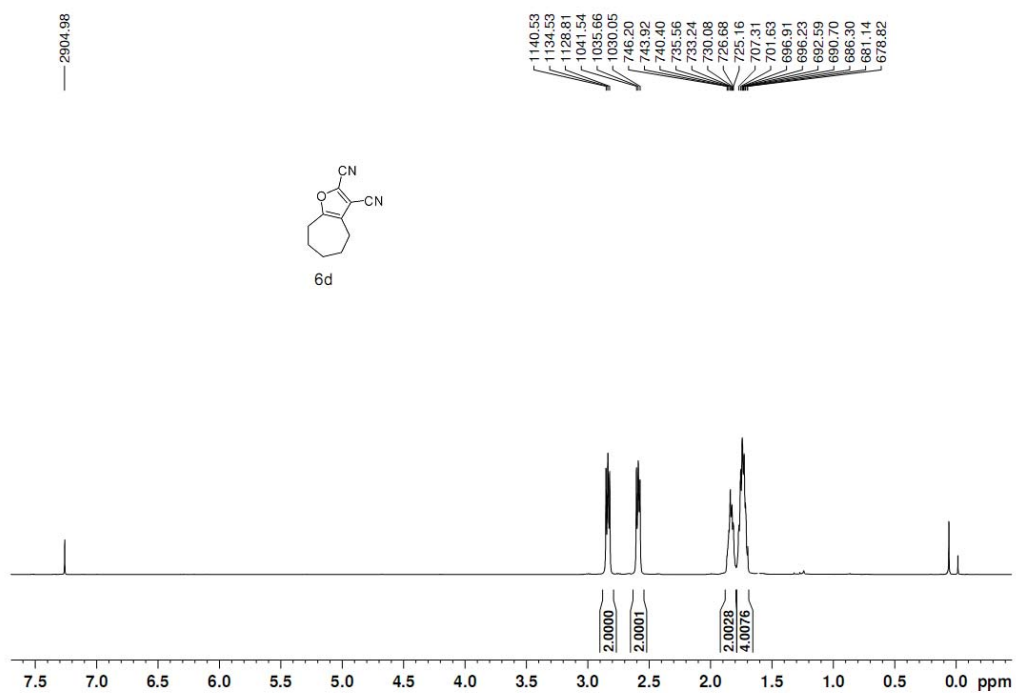


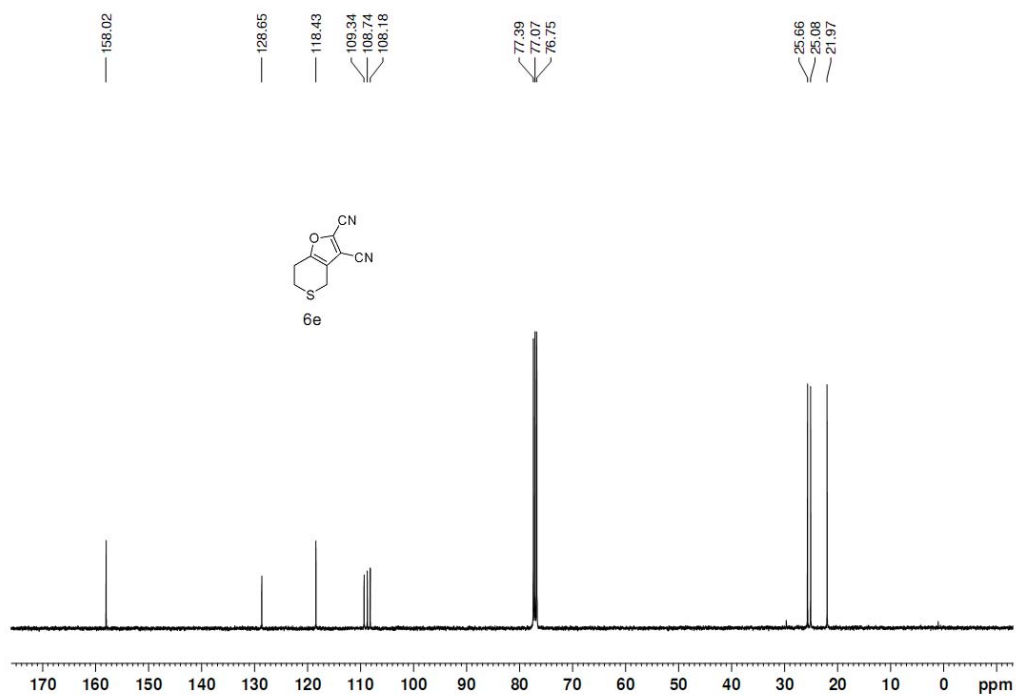
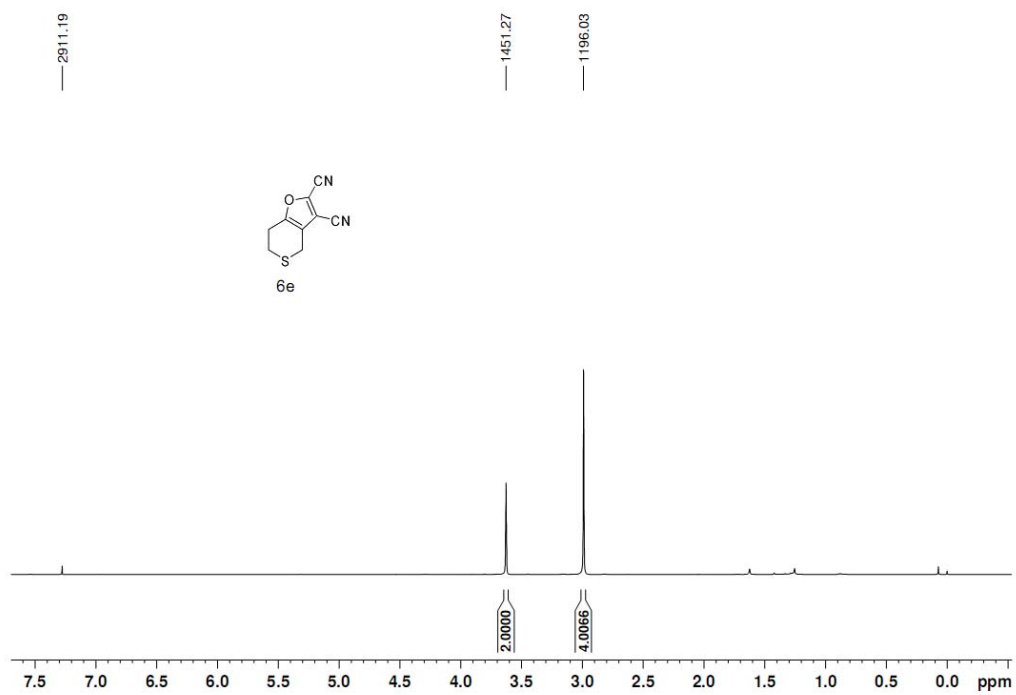


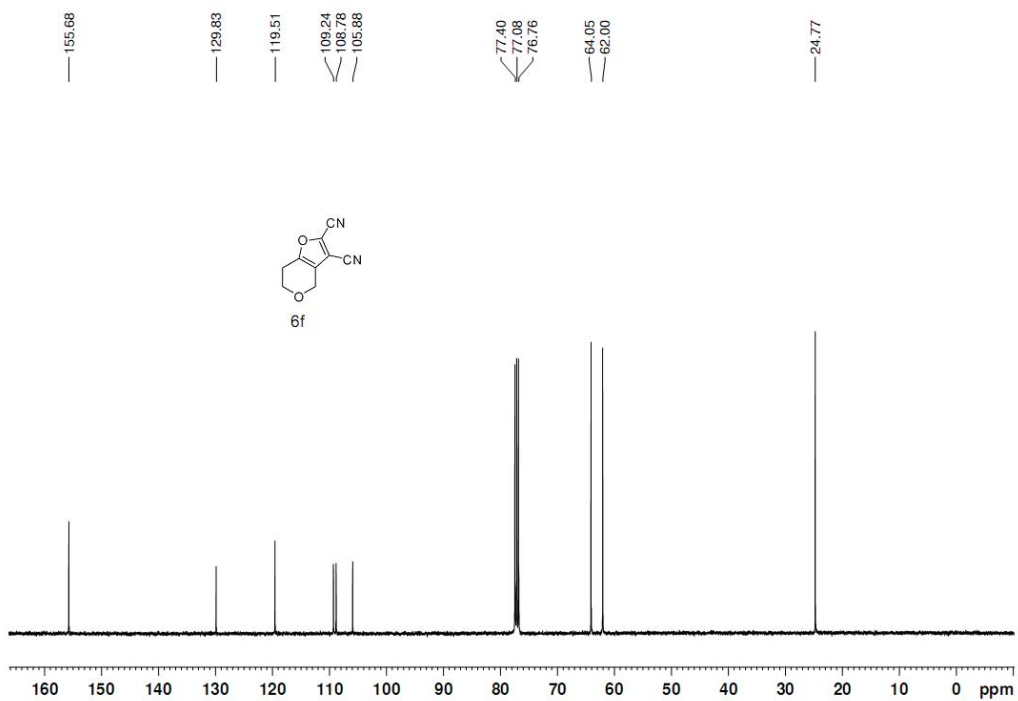
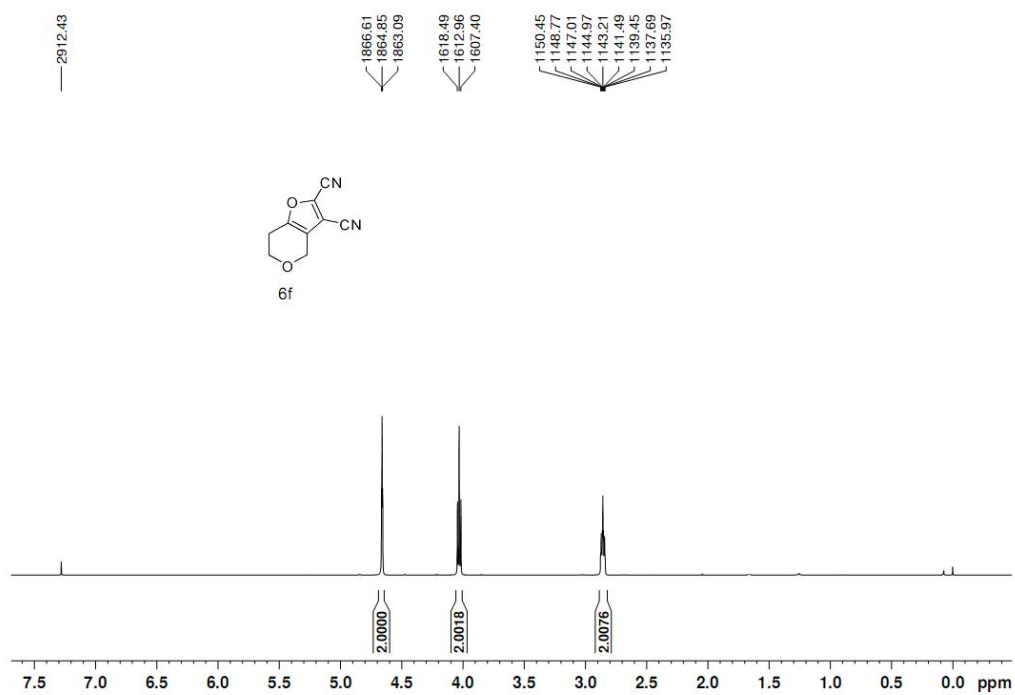


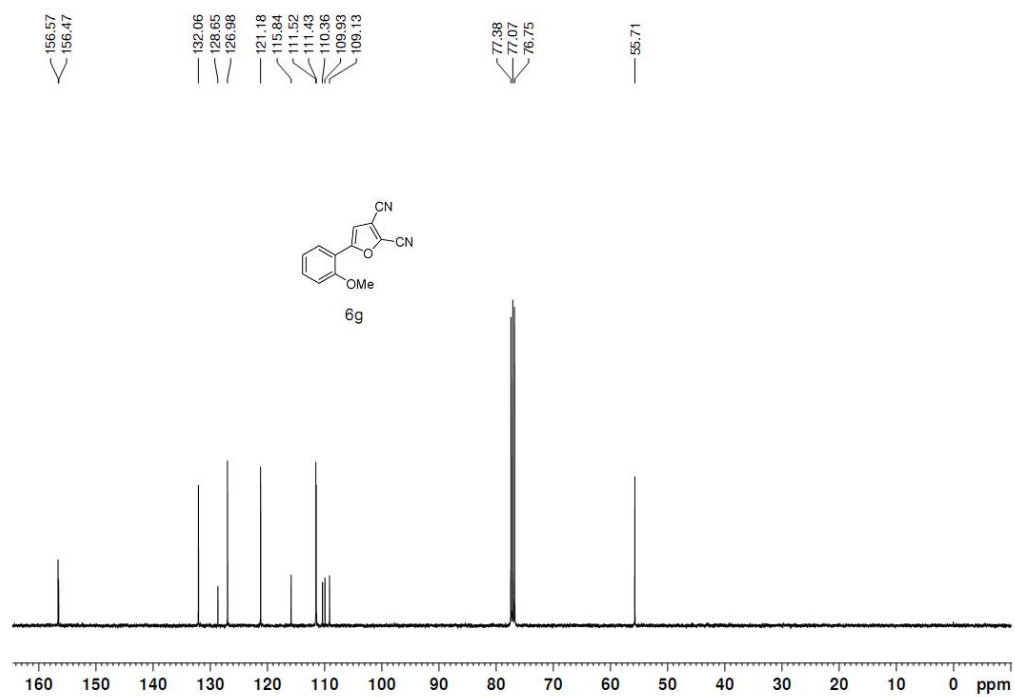
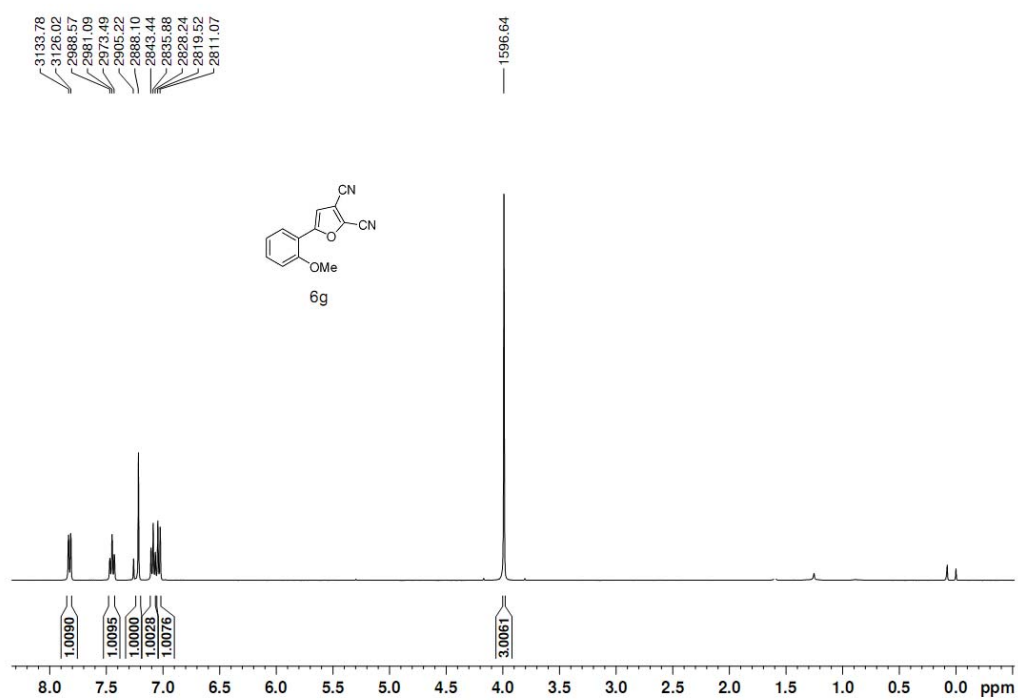


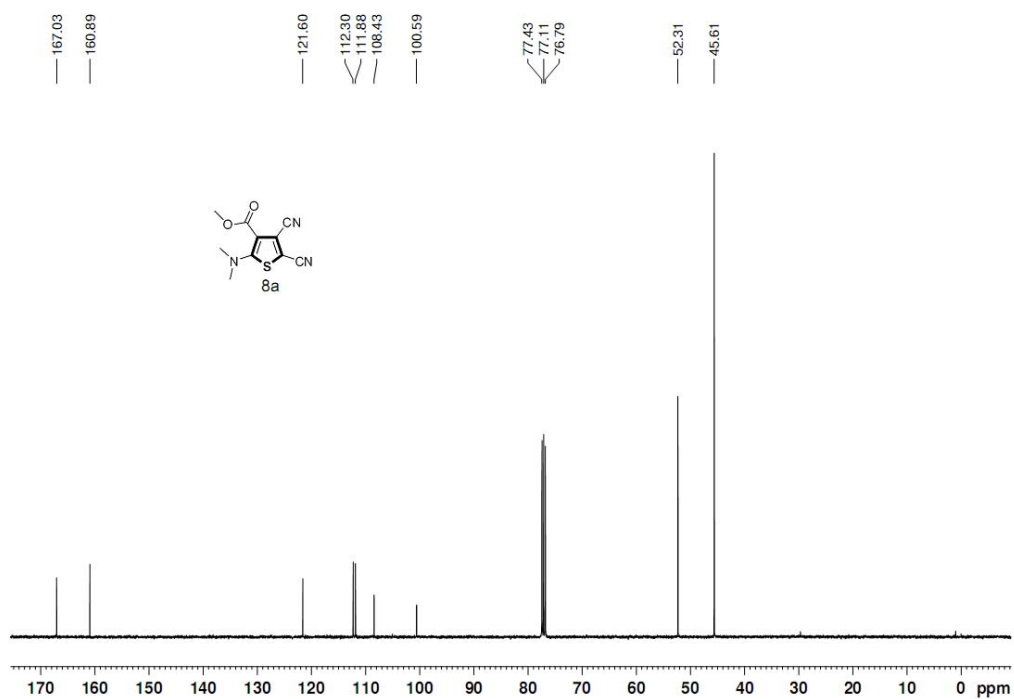
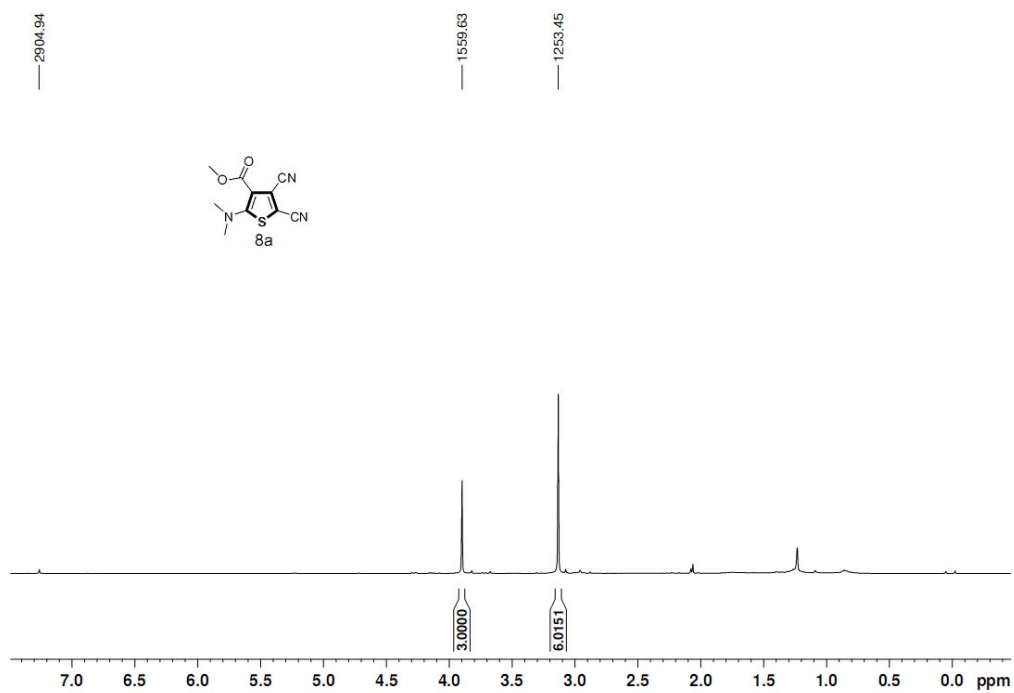


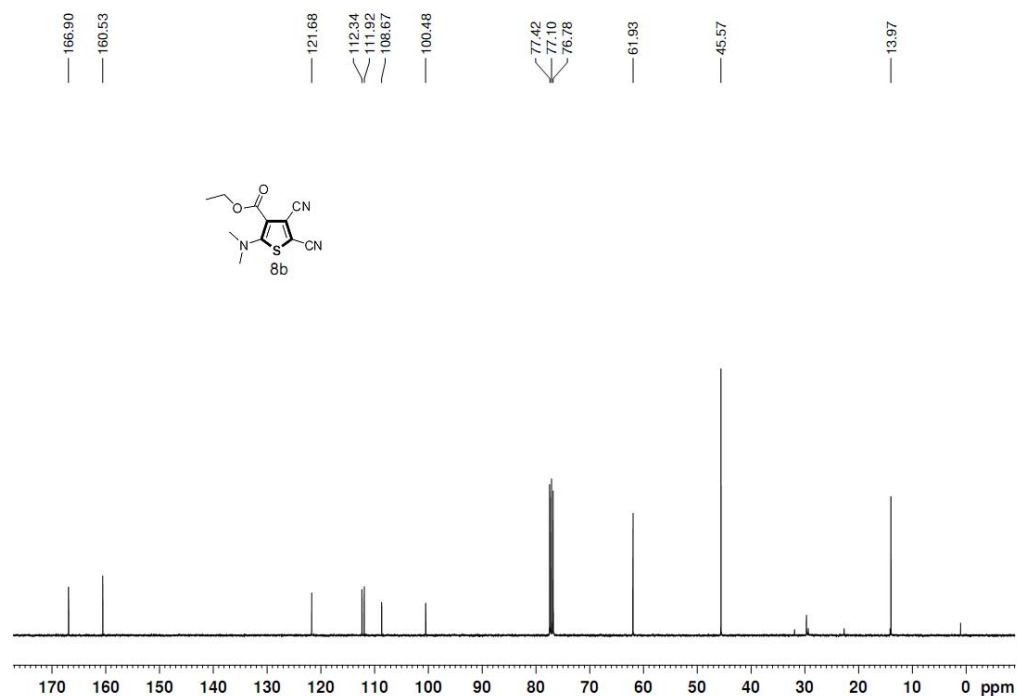
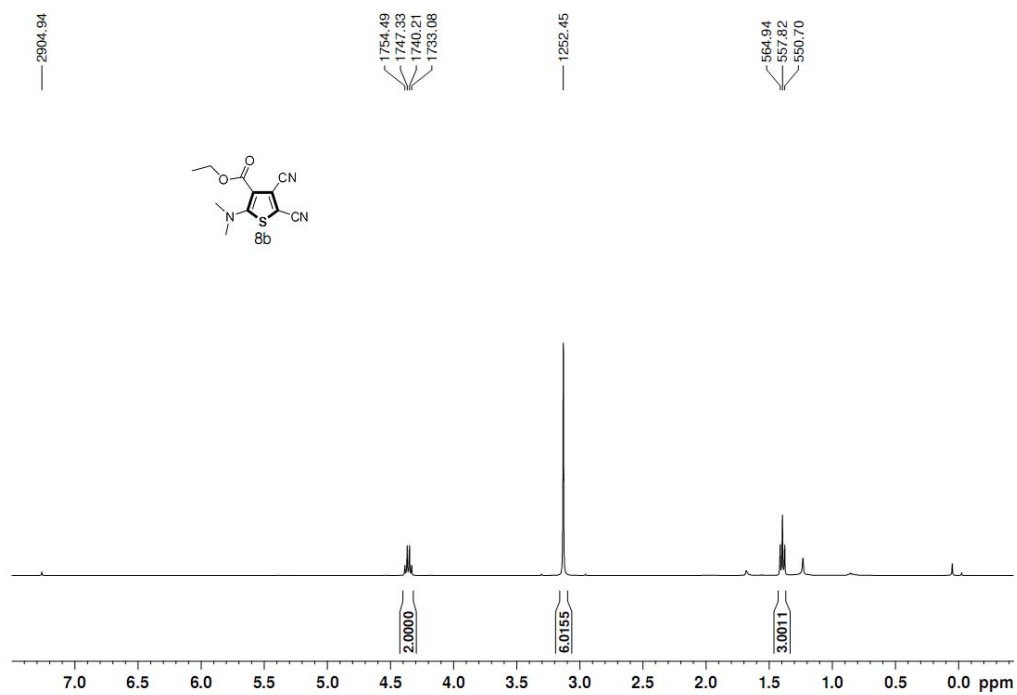


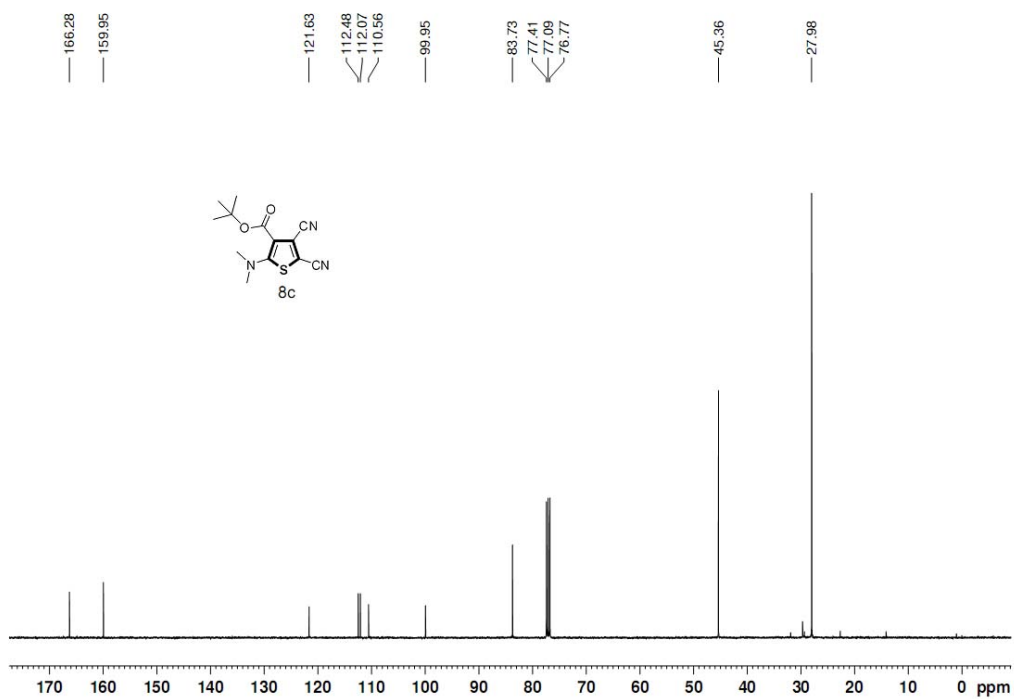
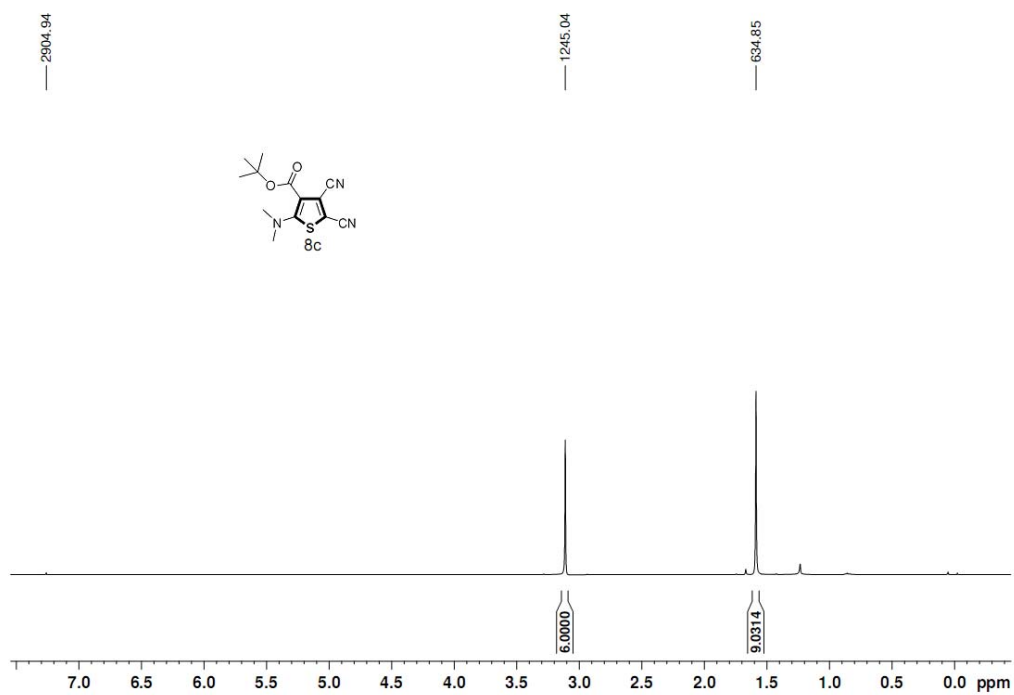


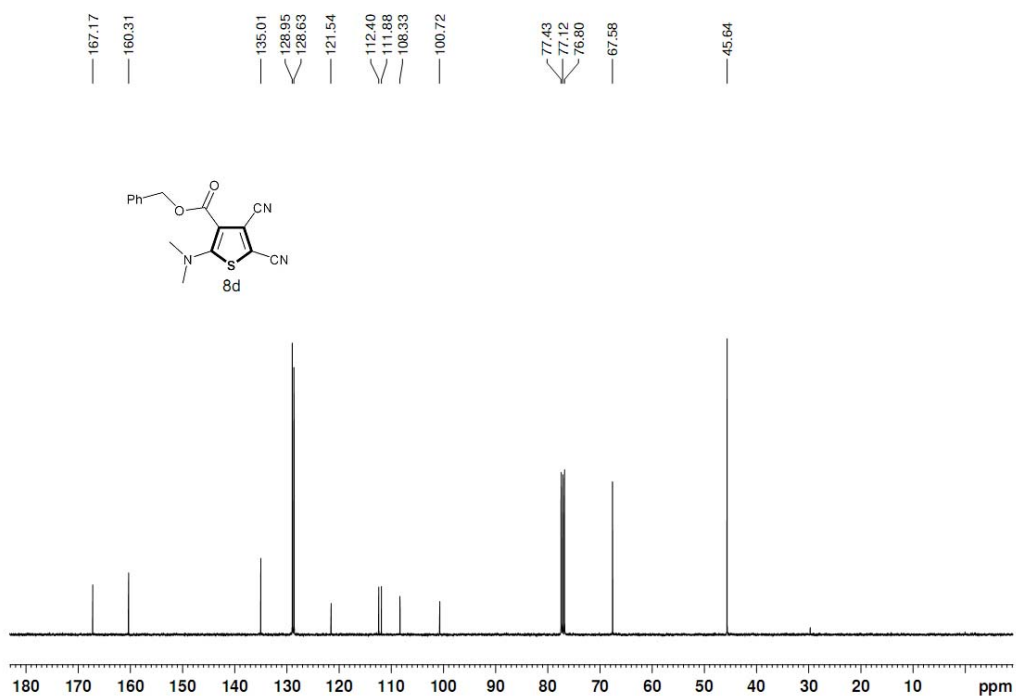
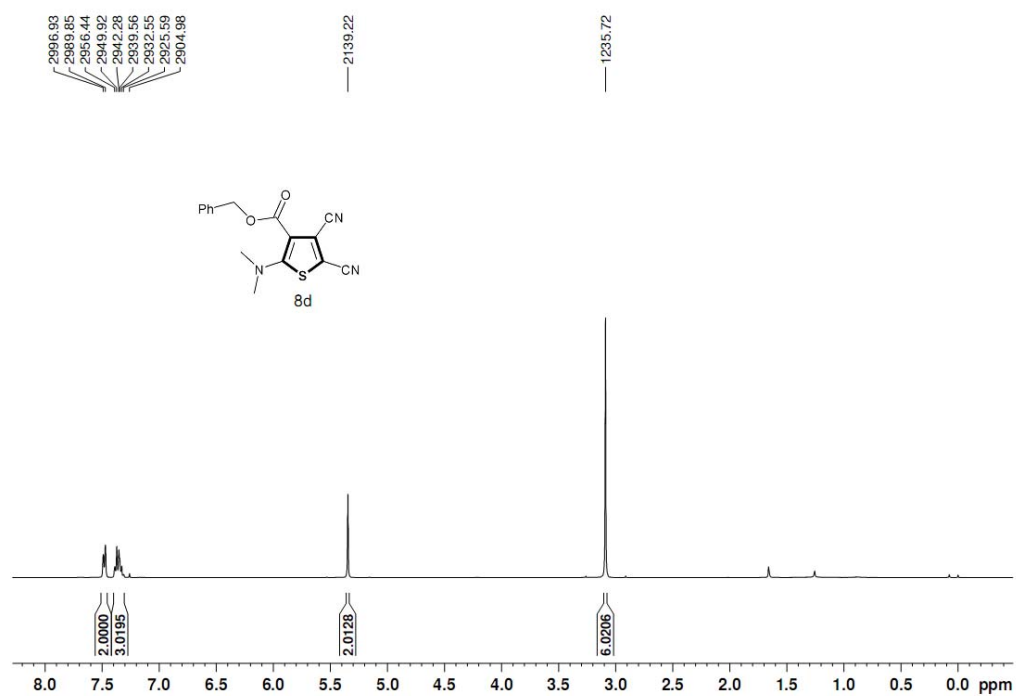


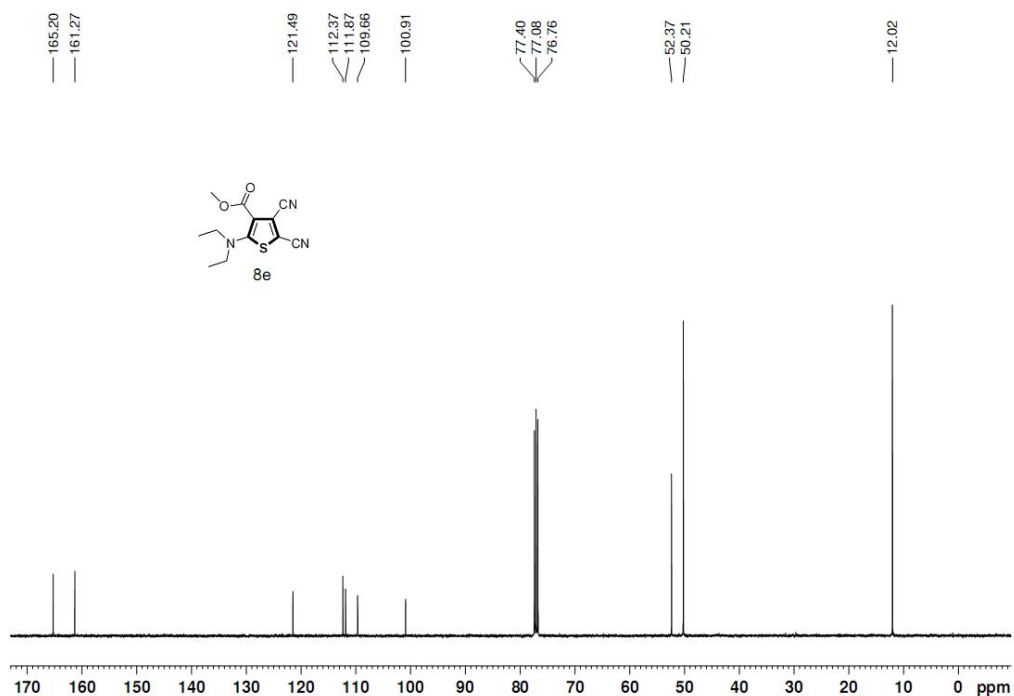
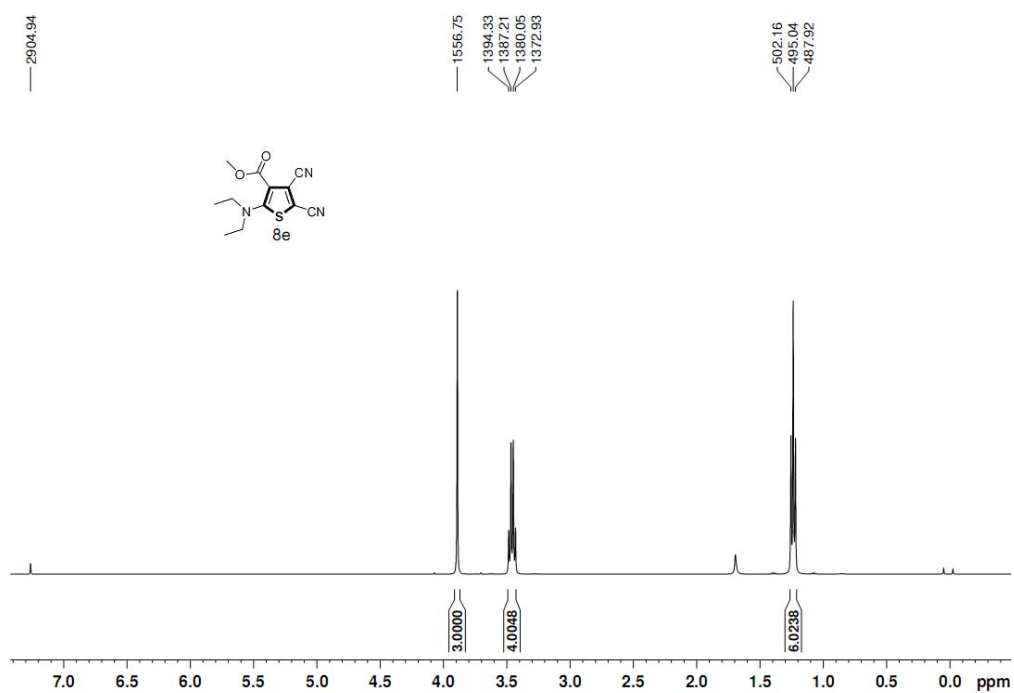


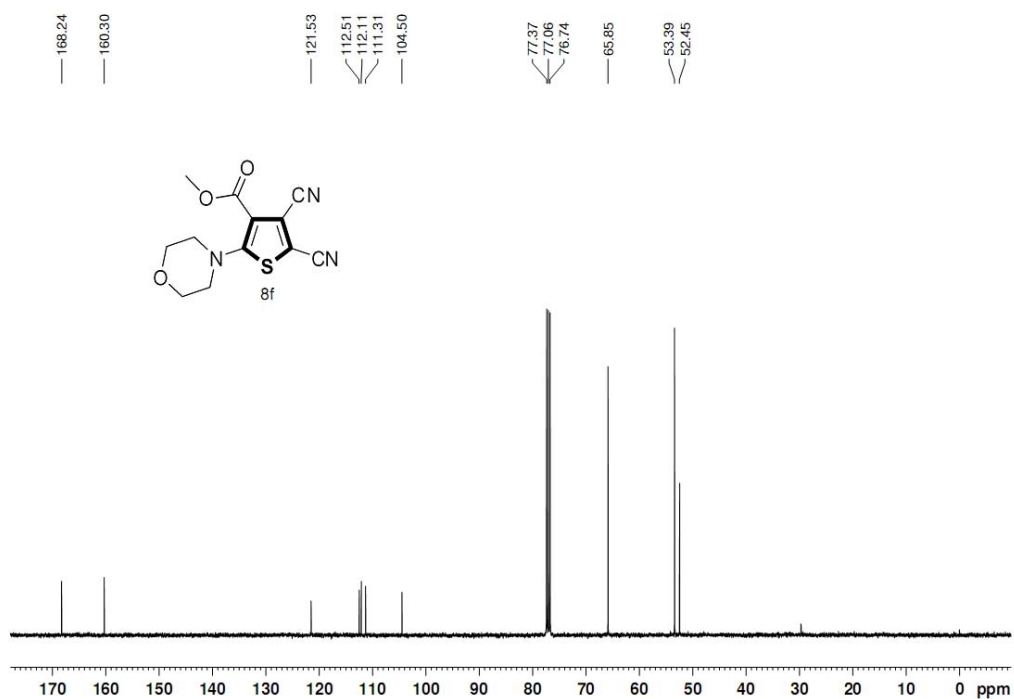
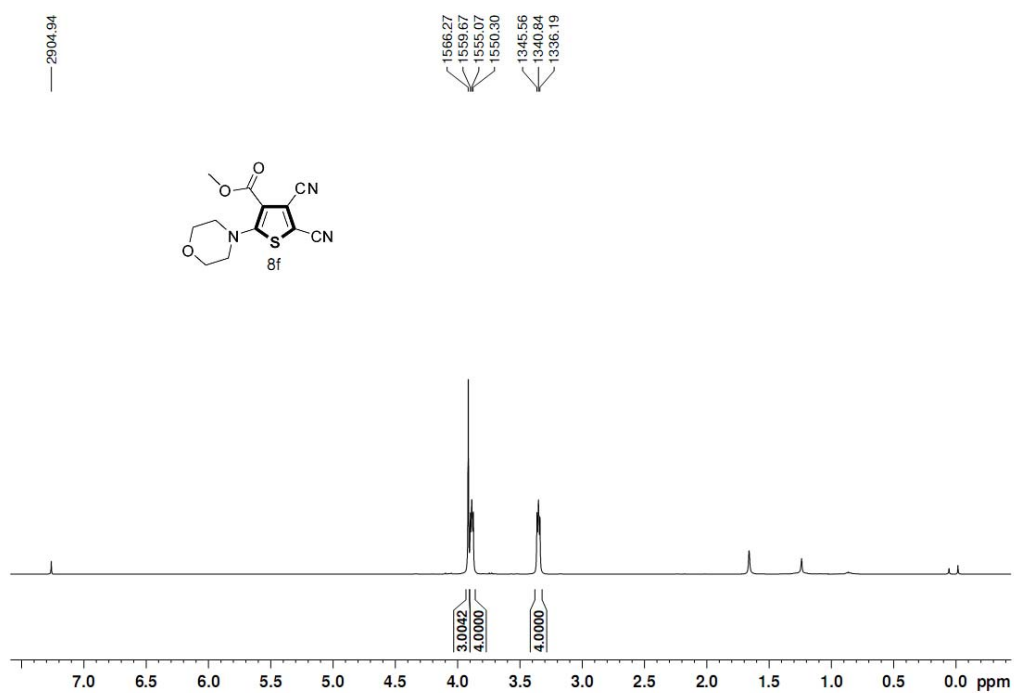


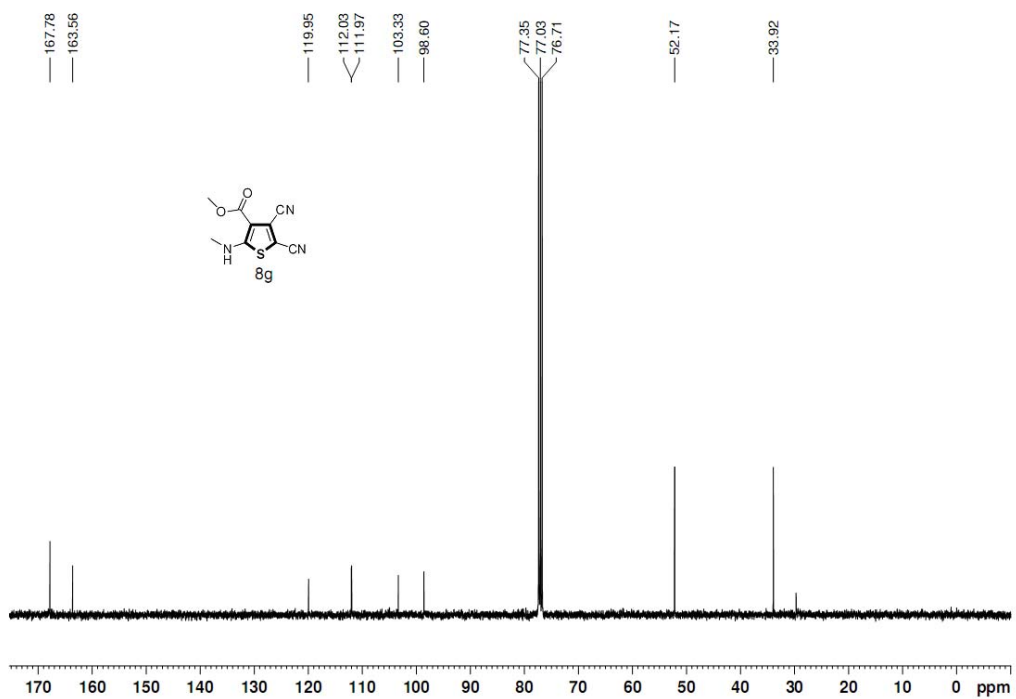
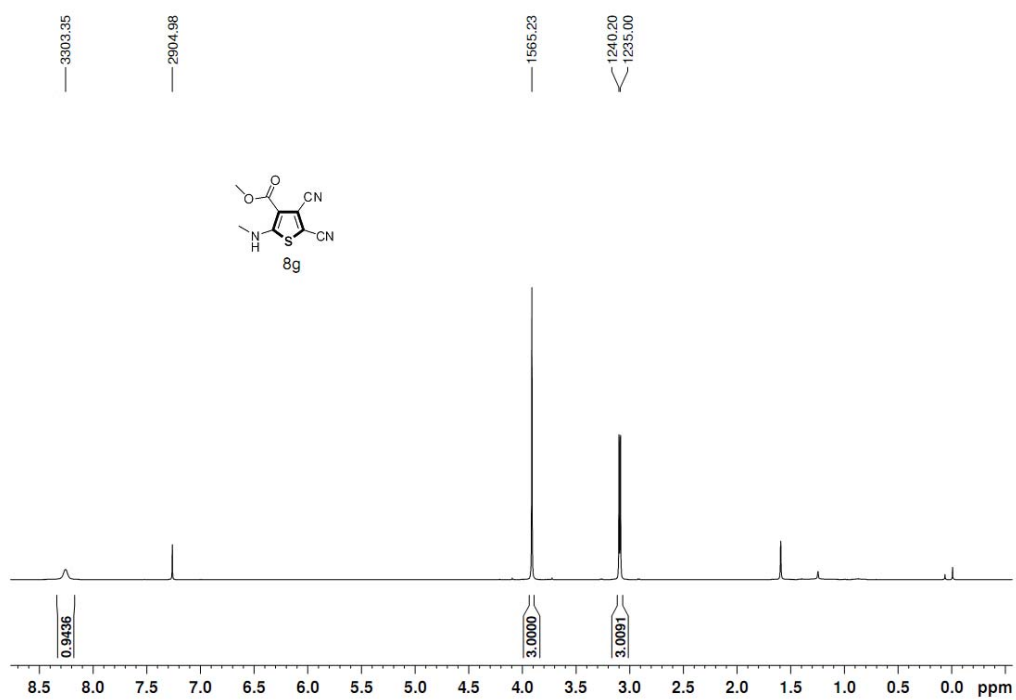


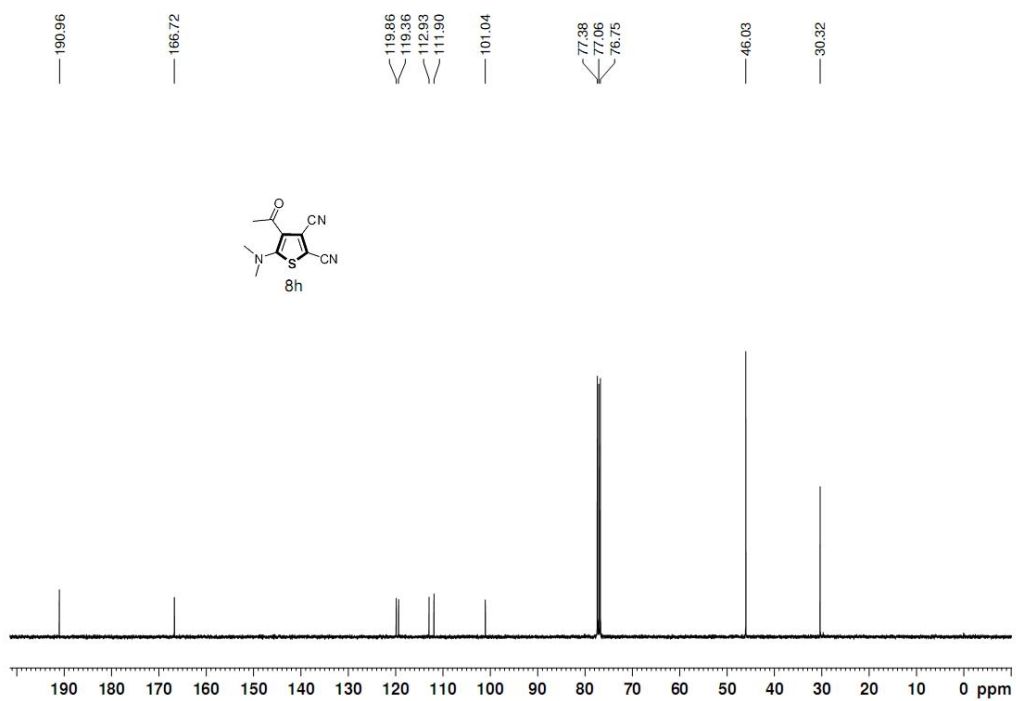
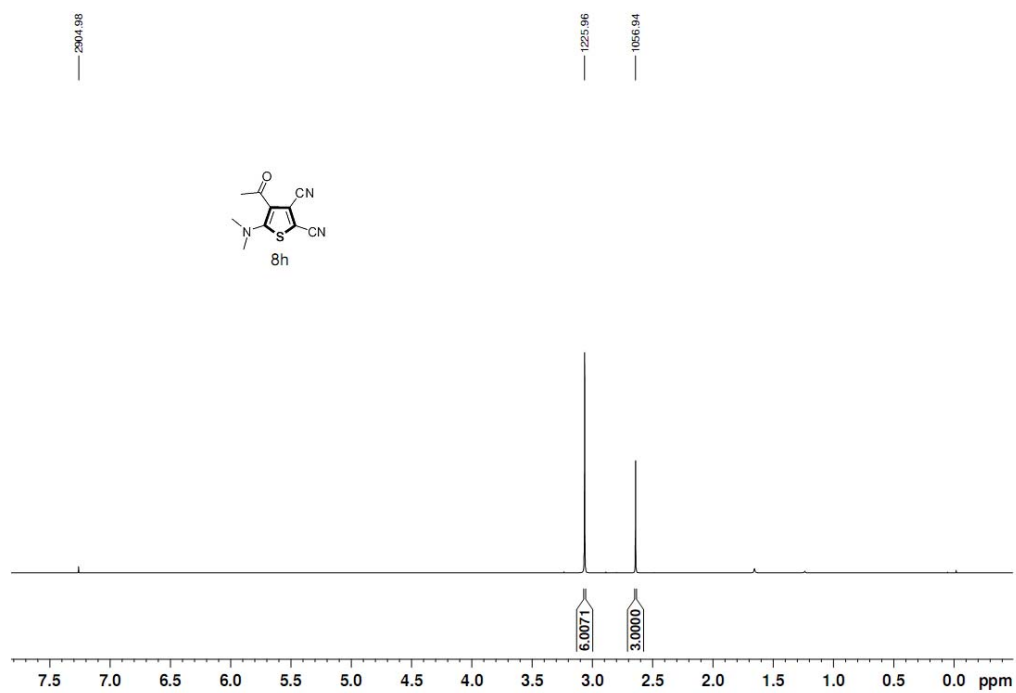


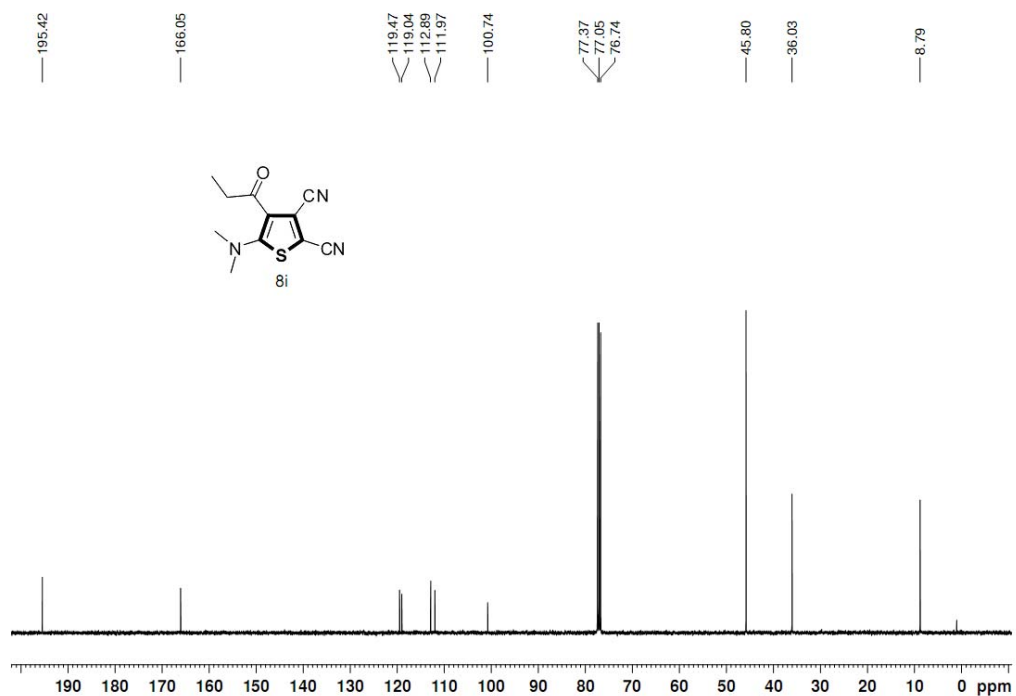
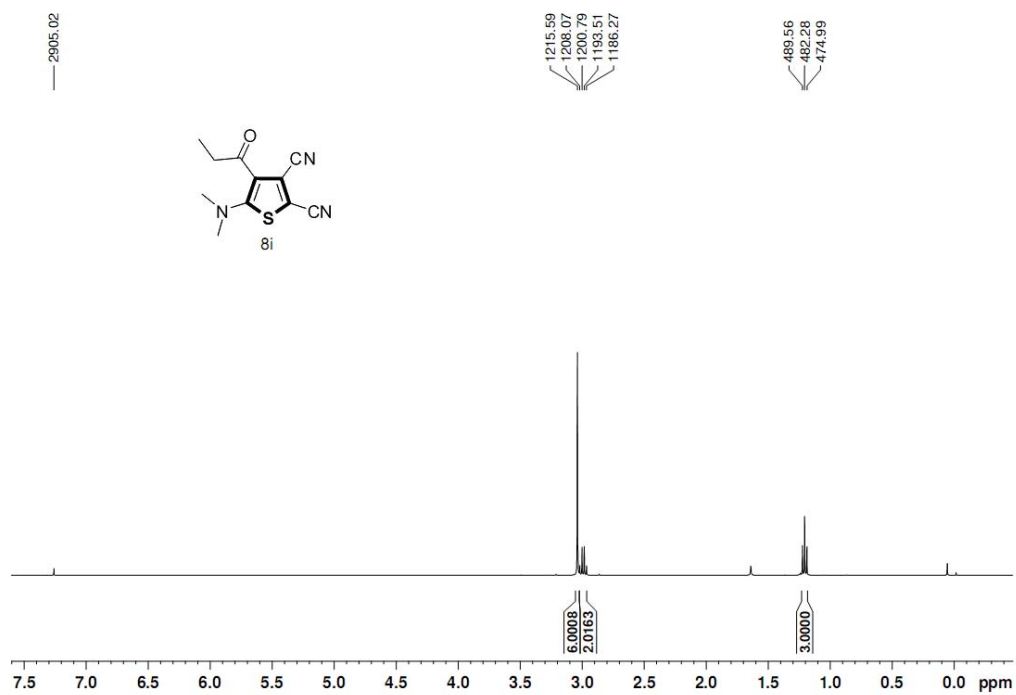


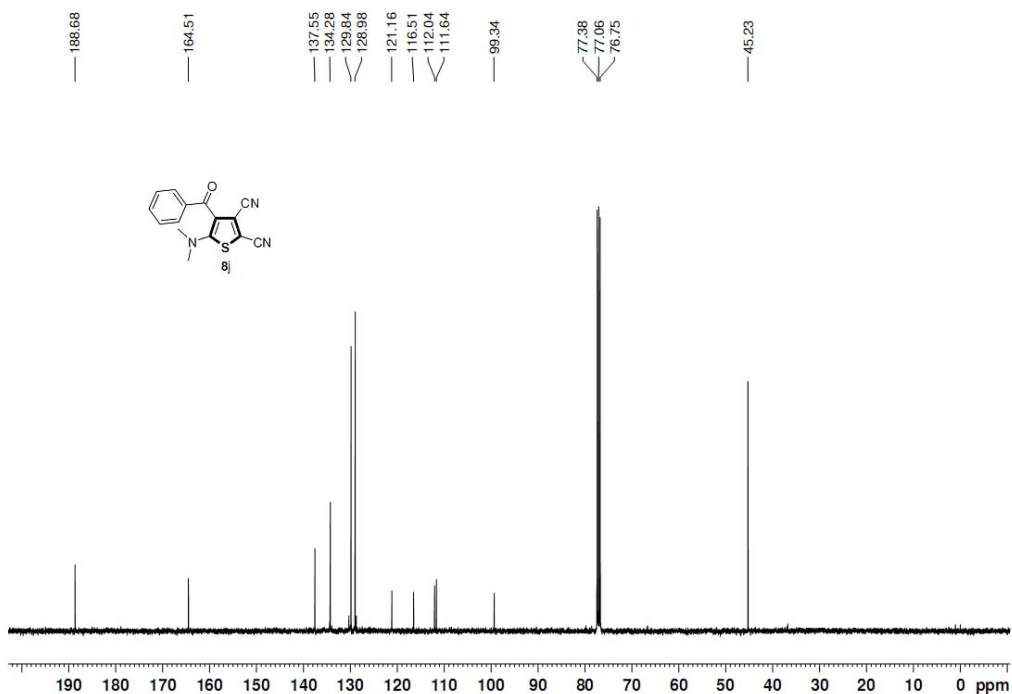
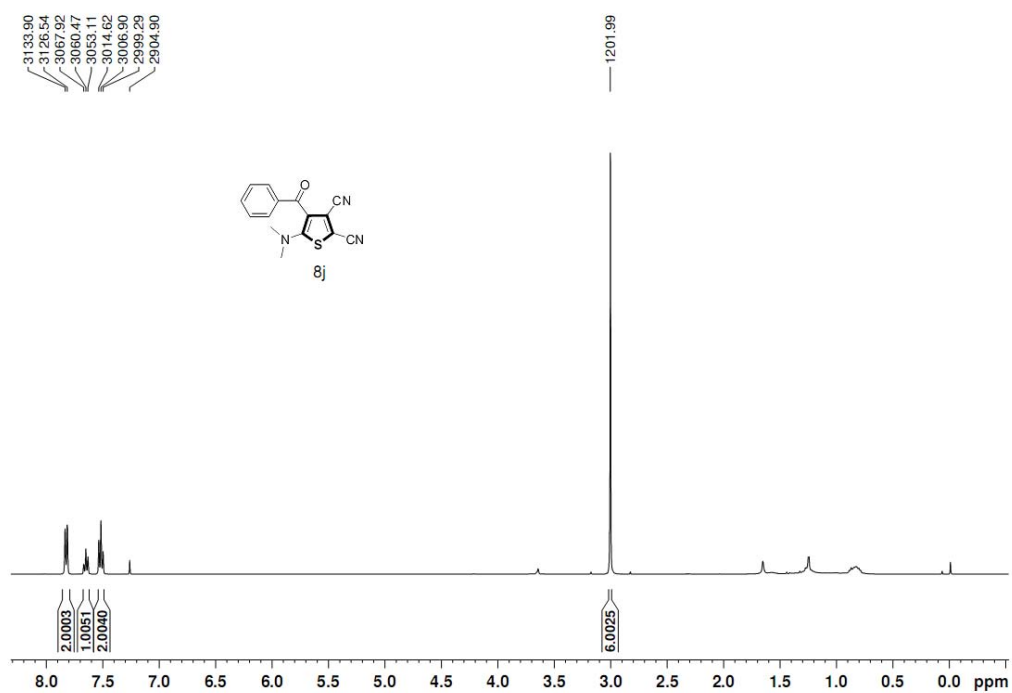


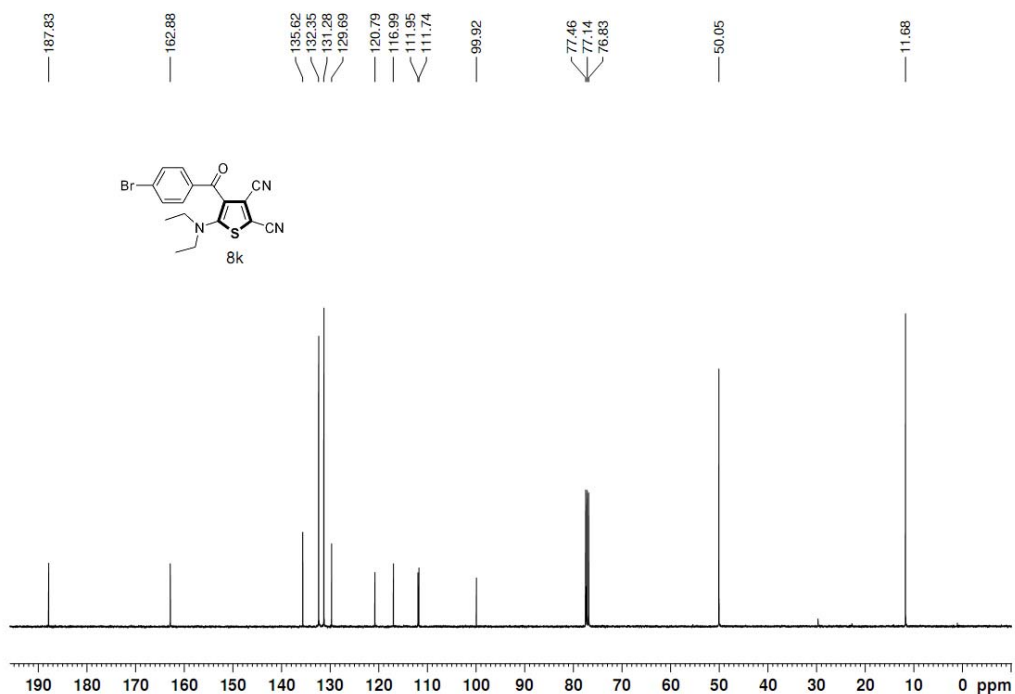
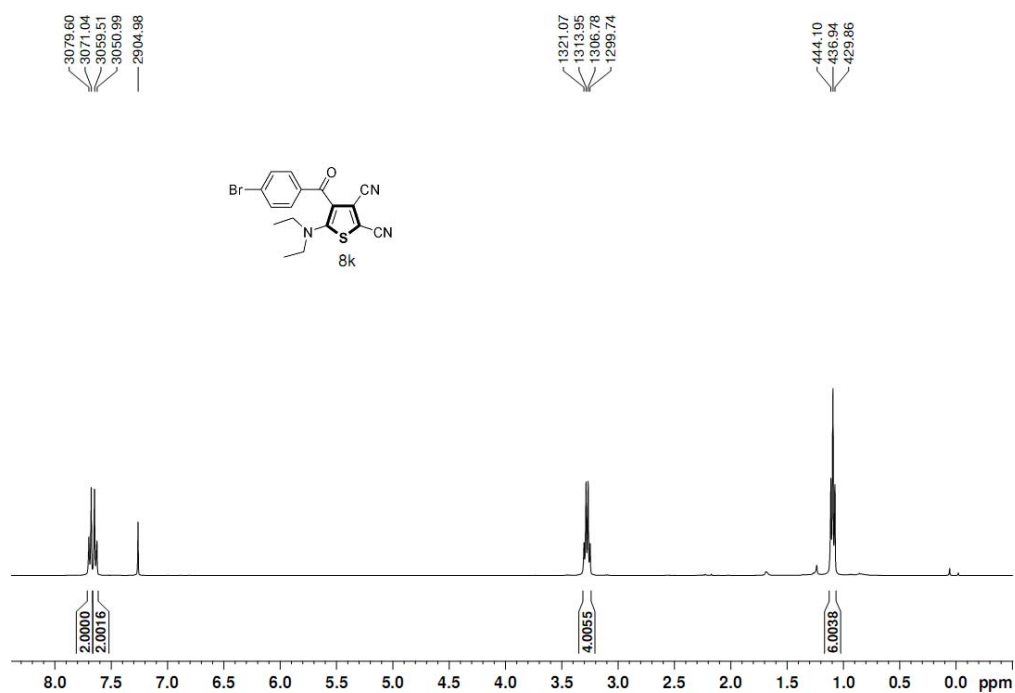


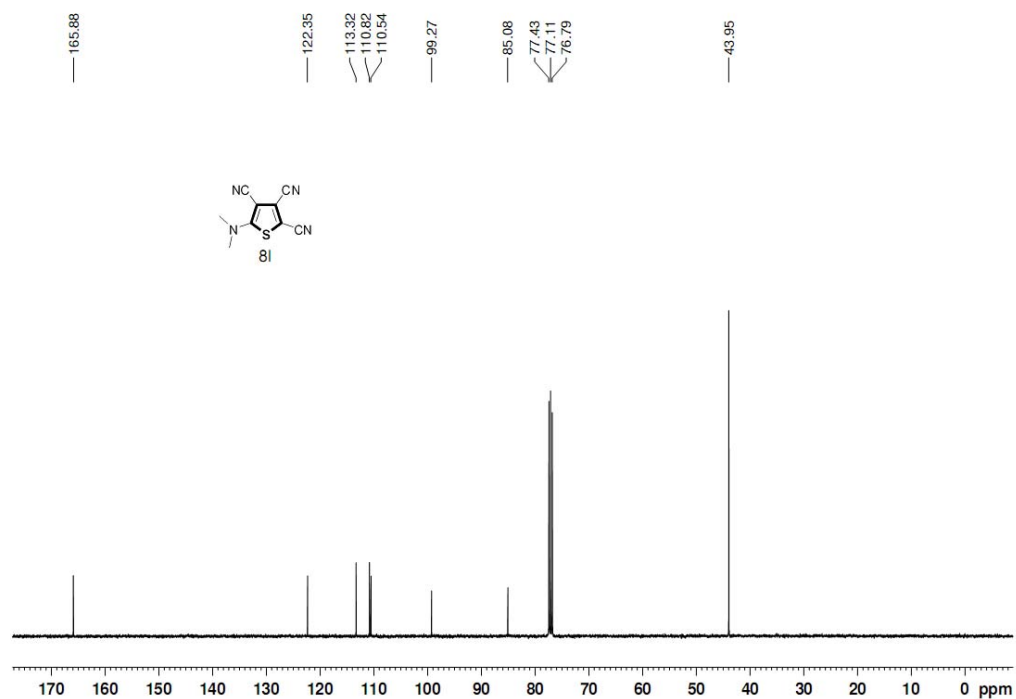
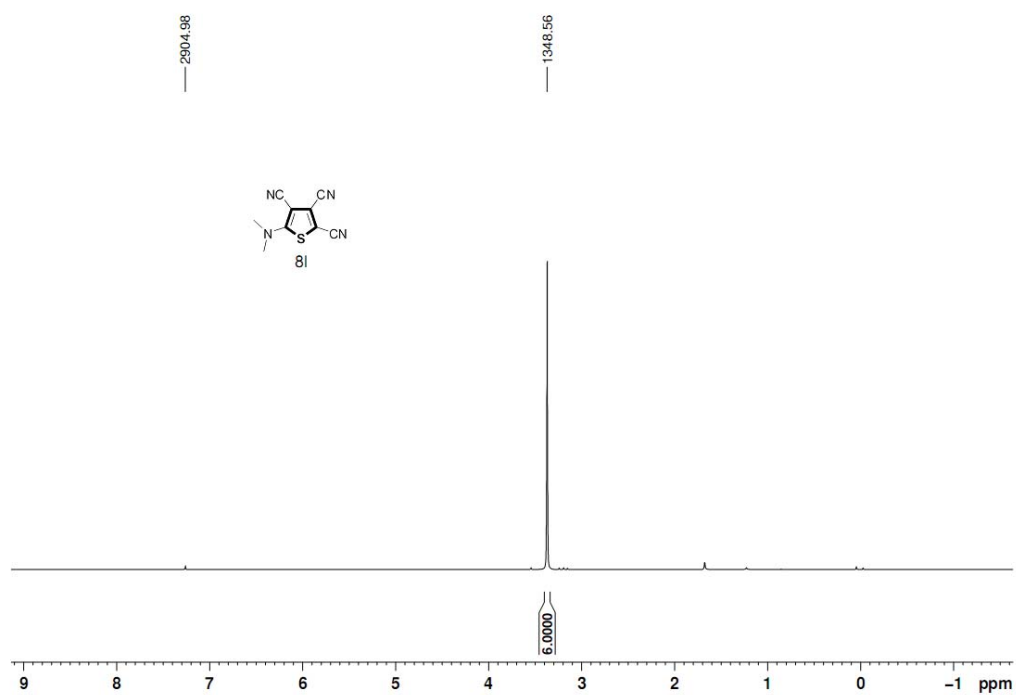


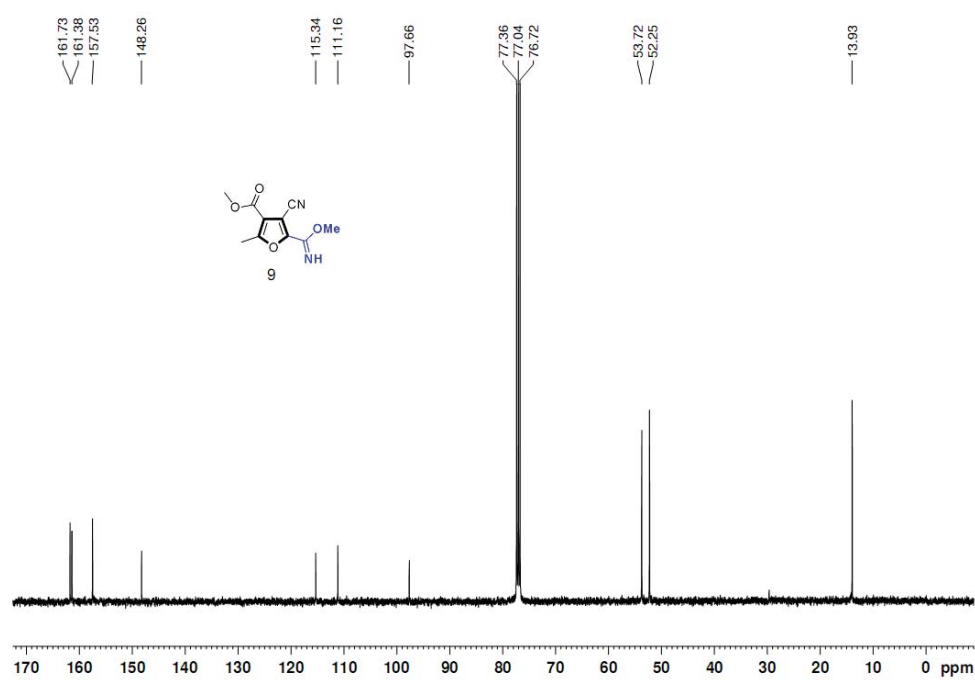
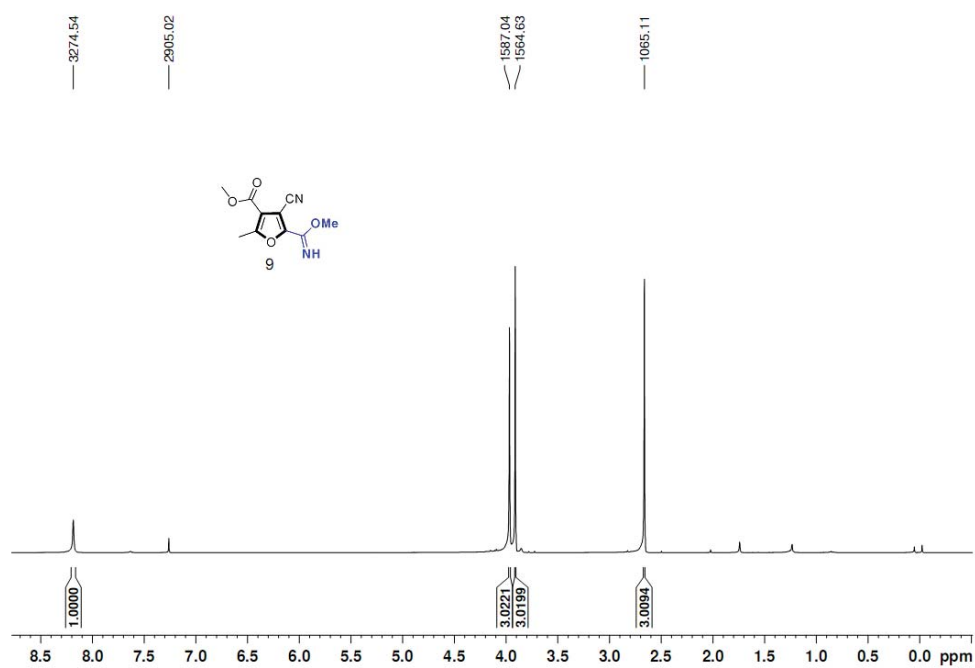


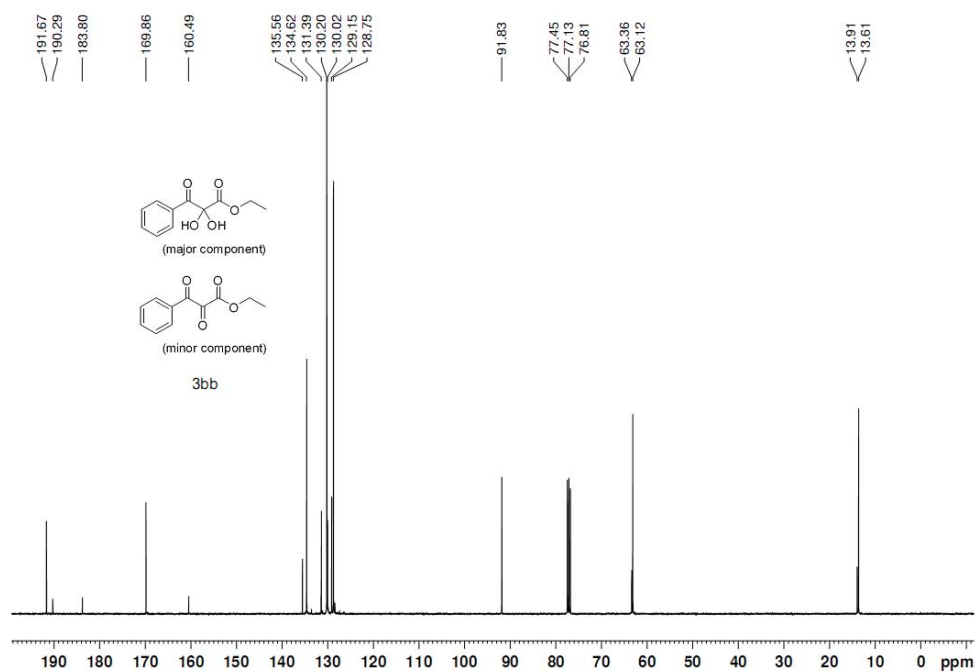
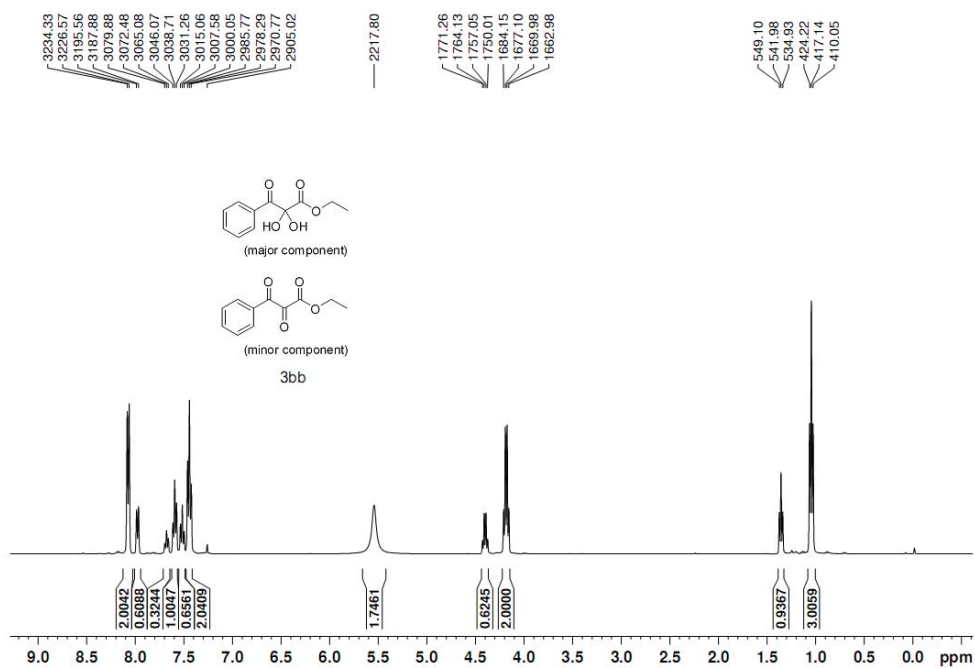












6. X-ray structure of **4k**, **8j** and **9** and the corresponding data

CCDC 943604 (**4k**), CCDC 943606 (**8j**) and CCDC 943605 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

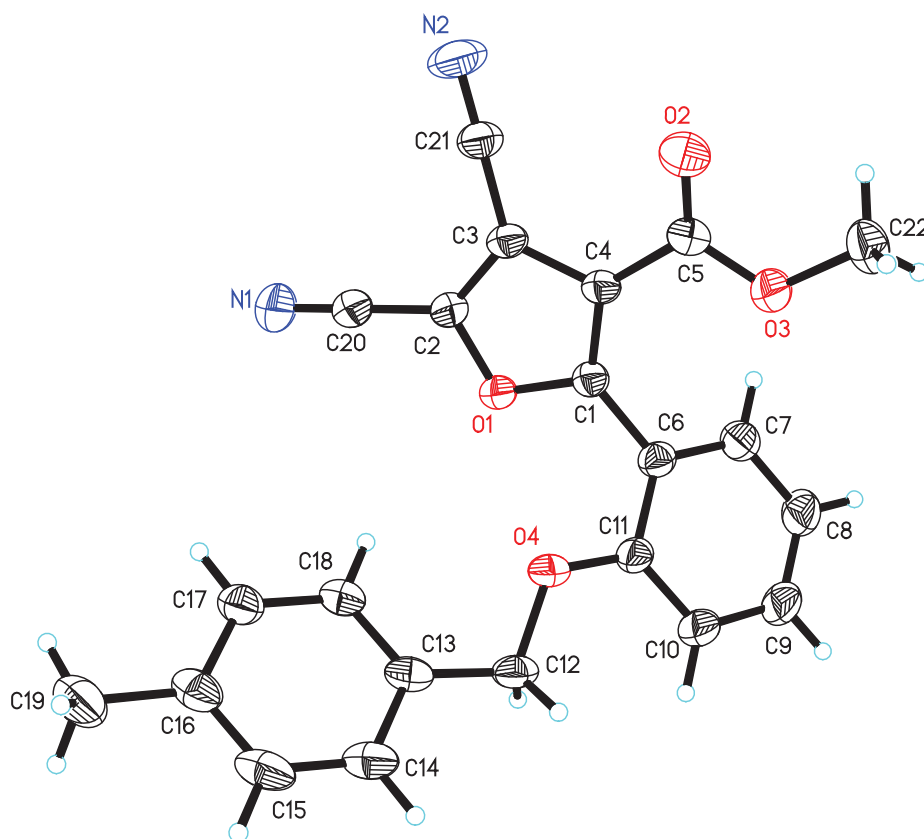


Figure S11. X-ray crystal structure of **4k**. Displacement ellipsoids are drawn at the 30% probability level.

Crystal data and structure refinement for **4k**

The X-ray crystallography data of **4k** are listed below: a colorless monoclinic crystal from n-hexane /ethyl acetate (3:1) was slowly exposed to graphite-monochromated Mo K α irradiation. The structures were solved by direct methods and refined on F^2 using all the reflections.

Empirical formula	C ₂₂ H ₁₆ N ₂ O ₄
Formula weight	372.37
Temperature	293 (2) K
Wavelength	0.71073 Å

Crystal system, space group	Monoclinic, P2 (1)
Unit cell dimensions	$a = 10.7714 (11) \text{ \AA}$ $\alpha = 90 \text{ deg.}$ $b = 7.8126(8) \text{ \AA}$ $\beta = 106.574(2) \text{ deg.}$ $c = 11.5206(12) \text{ \AA}$ $\gamma = 90 \text{ deg.}$
Volume	$929.21 (17) \text{ \AA}^3$
Z, Calculated density	2, 1.331 Mg /m^3
Absorption coefficient	0.093 mm^{-1}
F (000)	388
Crystal size	$0.356 \times 0.308 \times 0.257 \text{ mm}$
Theta range for data collection	$1.84 \text{ to } 26.00 \text{ deg.}$
Limiting indices	$-13 \leq h \leq 12, -9 \leq k \leq 9, -9 \leq l \leq 14$
Reflections collected / unique	5094 / 3426 [R (int) = 0.0154]
Completeness to $\theta = 26.00$	99.3%
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.72007
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3426 / 2 / 256
Goodness-of-fit on F^2	1.067
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0346, wR2 = 0.0943$
R indices (all data)	$R1 = 0.0387, wR2 = 0.0977$
Absolute structure parameter	1.7 (9)
Extinction coefficient	$0.106(7)$
Largest diff. peak and hole	$0.125 \text{ and } -0.132 \text{ e. \AA}^{-3}$

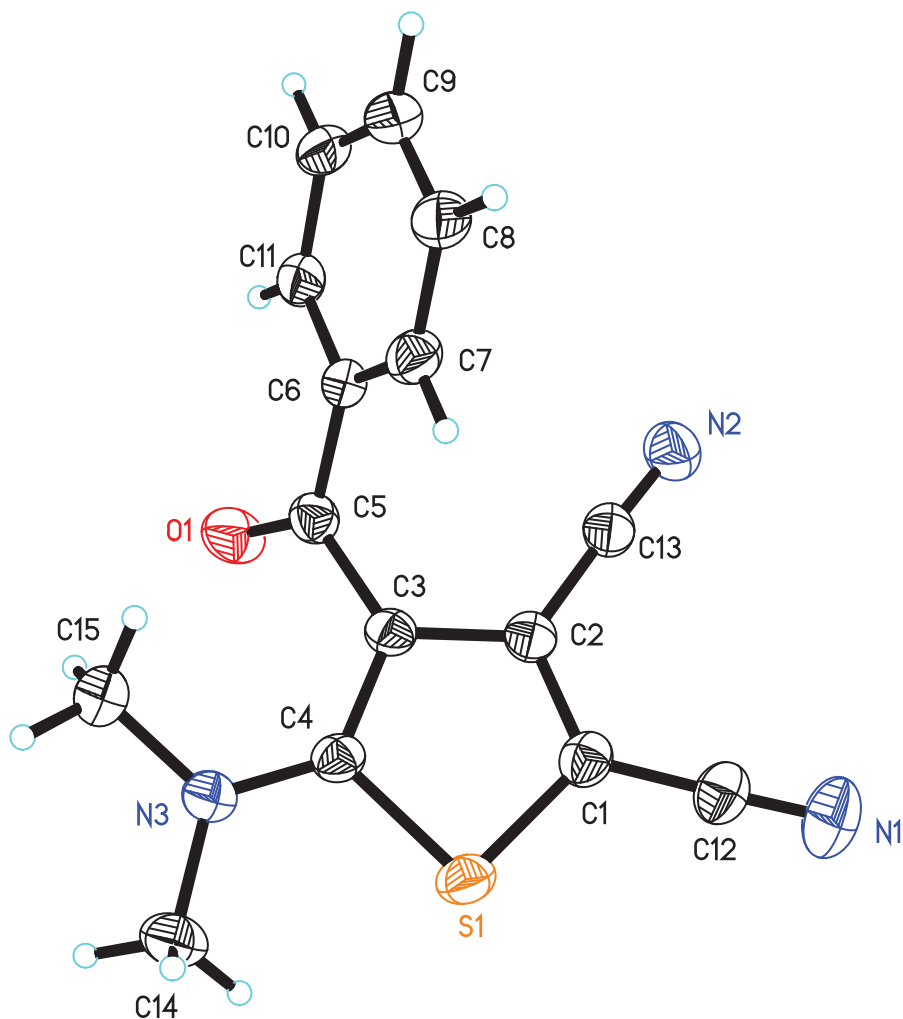


Figure S12. X-ray crystal structure of **8j**. Displacement ellipsoids are drawn at the 30% probability level.

Crystal data and structure refinement for **8j**

The X-ray crystallography data of **8j** are listed below: a yellowish monoclinic crystal from n-hexane /ethyl acetate/dichloroform (1:1:1) was slowly exposed to graphite-monochromated Mo K α irradiation. The structures were solved by direct methods and refined on F^2 using all the reflections.

Empirical formula	C ₁₅ H ₁₁ N ₃ OS
Formula weight	281.33
Temperature	293 (2) K

Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	$a = 8.1738(11)$ Å $\alpha = 90$ deg. $b = 21.296(3)$ Å $\beta = 109.477(3)$ deg. $c = 8.4023(11)$ Å $\gamma = 90$ deg.
Volume	$1378.9(3)$ Å ³
Z, Calculated density	4, 1.355 Mg /m ³
Absorption coefficient	0.233 mm^{-1}
F (000)	584
Crystal size	$0.212 \times 0.154 \times 0.112$ mm
Theta range for data collection	1.91 to 25.50 deg.
Limiting indices	$-9 \leq h \leq 8$, $-25 \leq k \leq 25$, $-9 \leq l \leq 10$
Reflections collected / unique	7757 / 2567 [R (int) = 0.0563]
Completeness to $\theta = 25.50$	100.0 %
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.20751
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2567 / 0 / 184
Goodness-of-fit on F^2	1.068
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0573$, $wR2 = 0.1382$
R indices (all data)	$R1 = 0.0635$, $wR2 = 0.1445$
Extinction coefficient	$0.046(5)$
Largest diff. peak and hole	0.343 and -0.370 e. Å ⁻³

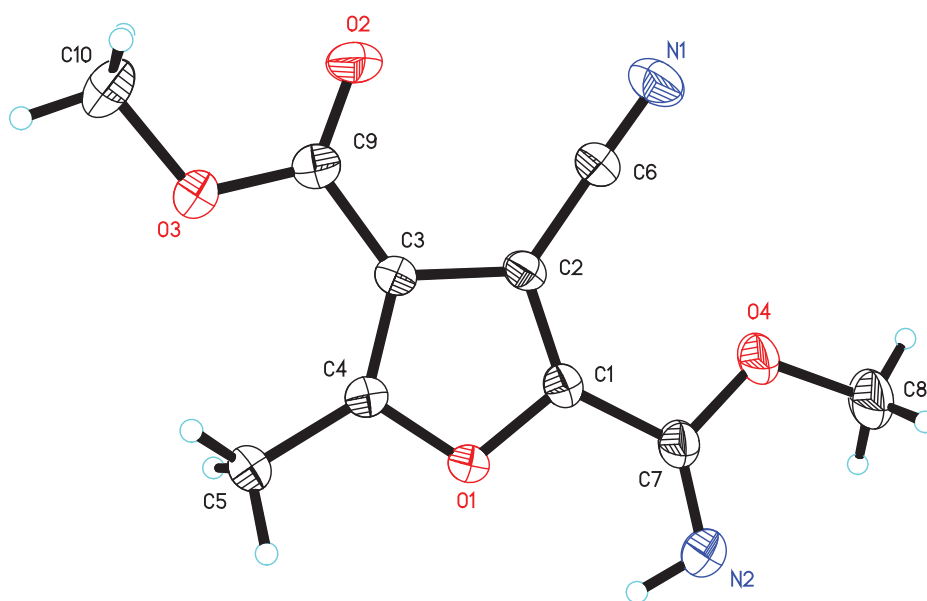


Figure S13. X-ray crystal structure of **9**. Displacement ellipsoids are drawn at the 30% probability level.

Crystal data and structure refinement for **9**

The X-ray crystallography data of **9** are listed below: a colorless Triclinic crystal from n-hexane /ethyl acetate (1:1) was slowly exposed to graphite-monochromated Mo K α irradiation. The structures were solved by direct methods and refined on F^2 using all the reflections.

Empirical formula	$\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}_4$	
Formula weight	222.20	
Temperature	293 (2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Triclinic, P-1	
Unit cell dimensions	$a = 7.107$ (2) Å	$\alpha = 75.924$ (5) deg.
	$b = 7.758$ (2) Å	$\beta = 79.636$ (6) deg.
	$c = 10.620$ (3) Å	$\gamma = 71.112$ (6) deg.
Volume	534.1 (3) Å ³	
Z, Calculated density	2, 1.382 Mg /m ³	
Absorption coefficient	0.109 mm ⁻¹	
F (000)	232	
Crystal size	$0.254 \times 0.187 \times 0.076$ mm	
Theta range for data collection	1.99 to 25.50 deg.	

Limiting indices	-8<=h<=8, -9<=k<=9, -12<=l<=11
Reflections collected / unique	3047 / 1965 [R (int) = 0.0251]
Completeness to theta = 25.50	98.4%
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.30135
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1965 / 1 / 153
Goodness-of-fit on F ²	1.080
Final R indices [I>2sigma (I)]	R1 = 0.0690, wR2 = 0.1963
R indices (all data)	R1 = 0.0823, wR2 = 0.2092
Extinction coefficient	0.065(17)
Largest diff. peak and hole	0.318 and -0.327 e. Å ⁻³