Supporting Information

Metal-free Synthesis of Nitriles from Aldehydes and Ammonium by Visible-Light Photocatalysis

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Contents

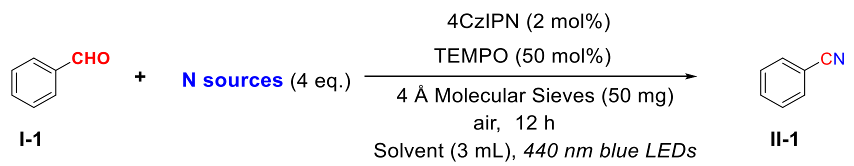
1. General Information

All reagents and solvents were commercially available unless individually noted. All the solvents used in photocatalyzed reactions were anhydrous solvents. Phenylmethanimine-BEt_3 and the 4CzIPN photocatalyst were prepared as previously reported [1-3]. The 440 nm blue LEDs were used as light sources. The products were isolated by silica column chromatograph (200-300 meshes silica gel). ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded using a Bruker Advance DPX instrument (400, 101 and 377 MHz, respectively) with tetramethylsilane (TMS) as an internal standard. Data for ^{1}H NMR was presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet, br = broad), coupling constant J (Hz) and integration. Data for ^{13}C NMR and ^{19}F NMR was reported in terms of chemical shift relative to different deuterium reagents. Mass spectra was recorded using a Trio-2000 GC-MS spectrometer. GC analysis was performed using He as the carrier gas with capillary column (30 m × 0.25 mm × 0.33 μm) and a flame ionization detector (FID) using *n*-tetradecane as an internal standard. Conversions and yields that were determined by ^{1}H NMR were obtained from the crude reaction mixture by using the diphenyl acetonitrile as an internal standard. UV-Vis absorption and luminescent quenching were performed on U-3900, F-4600 and LP-920. Cyclic voltammetry was performed on a CHI660E.

2. Experimental Procedures

2.1 The Optimization of Reaction Conditions

Table S1. The Optimization of Reaction Conditions [a)]



Entry	N Sources	Solvent	Yield of **II-1** [b)]
1	NH_4OAc [c)]	CH_3CN	75%
2	NH_2COONH_4	CH_3CN	39%
3	$(NH_4)_2CO_3$	CH_3CN	60%
4	NH_3(g)	CH_3CN	71%
5	NH_4Cl	CH_3CN	n.r.
6	NH_2OH•HCl	CH_3CN	n.d.
7	NH_2OH (50% aq. soln.)	CH_3CN	n.d.
8	NH_4OAc	CH_3OH	trace
9	NH_4OAc	EtOH	trace
10	NH_4OAc	DMF	trace
11	NH_4OAc	DCM	4%
12	NH_4OAc	THF	trace

a) Reactions were carried out at 0.2 mmol scale in 3 mL solvent with 2 mol% 4CzIPN, 50 mol% TEMPO, 4 equiv. nitrogen sources, 50 mg 4 Å molecular sieves under air upon 440 nm blue LEDs irradiation for 12 h. b) Yields were obtained from the crude and filtered reaction mixture by GC-FID with *n*-tetradecane as the internal standard. c) 2.5 equiv. NH_4OAc.

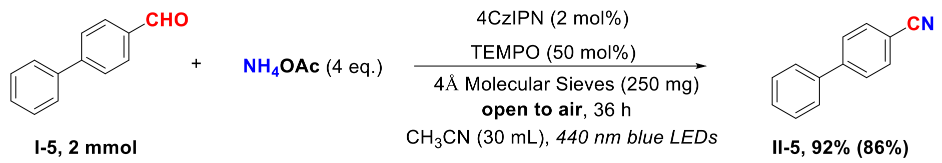
2.2 The General Procedure for Photoreaction

In an 8 mL reaction tube, 4CzIPN (4×10^{-3} mmol, 3.16 mg), NH_4OAc (0.8 mmol. 61.7 mg), TEMPO (Cocat.) (0.1 mmol, 15.6 mg) and 50 mg 4Å molecular sieves were dissolved and blended in 3 mL CH_3CN. And then the aldehyde (0.2 mmol) was added and the reaction mixture was vigorously stirred for 30 min before irradiation. After that, the mixture was exposed to air and irradiated at room temperature by use of 440 nm blue LEDs. Upon 12 h irradiation, the yield of nitrile was obtained from the filtrated crude reaction mixture by ^{1}H NMR or GC-FID using diphenyl acetonitrile or *n*-tetradecane as the internal standard.

2.3 Scaled-up Photoreaction

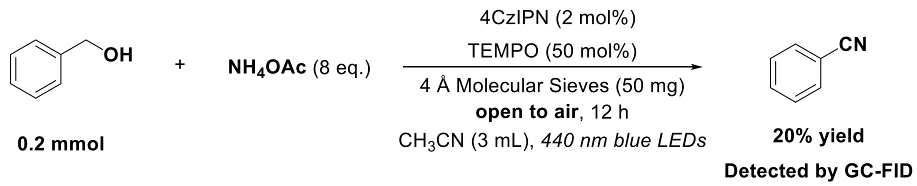
In a 100 mL round-bottom flask, 4CzIPN (4×10^{-2} mmol, 31.6 mg), NH_4OAc (8 mmol, 617 mg), TEMPO

(1 mmol, 156 mg) and 250 mg 4Å molecular sieves were dissolved and blended in 30 mL CH_3CN. And then the 4-biphenylcarboxaldehyde **I-5** (2 mmol, 364.4 mg) was added and the reaction mixture was vigorously stirred for 30 min before irradiation. After that, the mixture was exposed to air and irradiated at room temperature by use of 440 nm blue LEDs. Upon 36 h irradiation, the yield of [1,1'-biphenyl]-4-carbonitrile **II-5** was obtained from the filtrated crude reaction mixture by ^1H NMR using diphenyl acetonitrile as the internal standard. The crude product was purified by silica gel column chromatography (petroleum ether/DCM 5/1 to 2/1) to afford **II-5** as white solid (308.2 mg, 86% yield).



Scheme S1 The scaled-up experiment. ^1H NMR yield (isolated yield) were showed under the **II-5**.

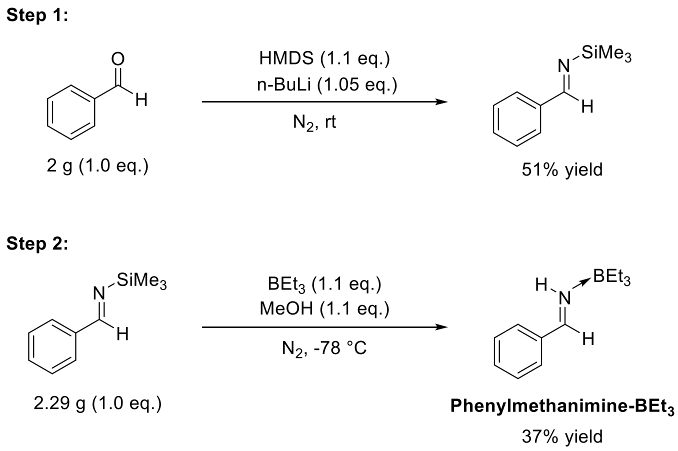
2.4 The Oxidation of the Alcohol to Nitrile



Scheme S2 The oxidation of the alcohol to nitrile.

2.5 The Synthesis of Phenylmethanimine-BEt_3

The Phenylmethanimine-BEt_3 was prepared as previously reported [1-2]. ^1H NMR (600 MHz, $CDCl_3$, ppm) δ: 9.34 (d, J = 21.4 Hz, 1H), 8.09 (d, J = 21.4 Hz, 1H), 7.68 – 7.52 (m, 5H), 0.75 (t, J = 7.8 Hz, 9H), 0.34 (t, J = 7.8 Hz, 6H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm) δ: -2.00.



Scheme S3 The synthesis of phenylmethanimine-BEt_3.

3. Mechanism Studies

3.1 Cyclic Voltammetry (CV) Experiments

A CH_3CN solution (3×10^{-4} M) of **I-1** and a CH_3CN solution (3×10^{-4} M) of TEMPO was prepared respectively with NBu_4PF_6 (0.1 M) as the supporting electrolyte. The cyclic voltammogram was obtained using a glassy carbon as working electrode, a Pt strip as counter electrode, and a saturated calomel electrode as reference electrode. Scan rate = 0.1 V/s, range from 0 V to 3.0 V.

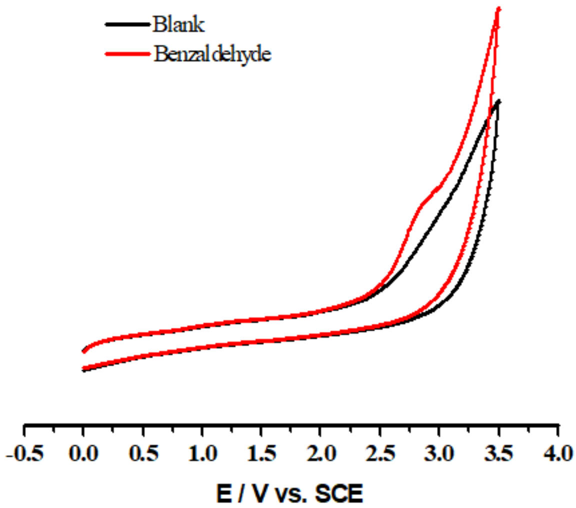


Figure S1 The cyclic voltammetry spectra of benzaldehyde **I-1** shows an oxidative potential at 2.83 V vs. SCE in CH_3CN.

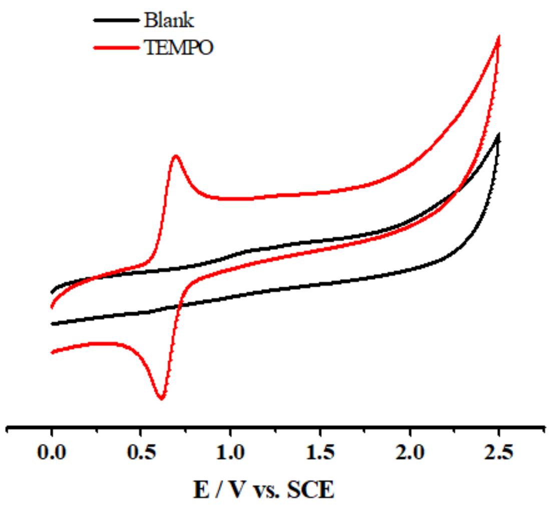


Figure S2 The cyclic voltammetry spectra of TEMPO in CH_3CN.

3.2 Spectroscopy Experiments

The mixed filtrate in **figure S3a** was prepared as follow. Benzaldehyde (0.2 mmol), NH_4OAc (0.8 mmol) and 4 Å MS (50 mg) were blended in CH_3CN (3 mL) and the mixture was stirred for 30 min, after that the molecular sieve was filtered out. The concentrations in **figure S3a** were calculated by the concentrations of benzaldehyde.

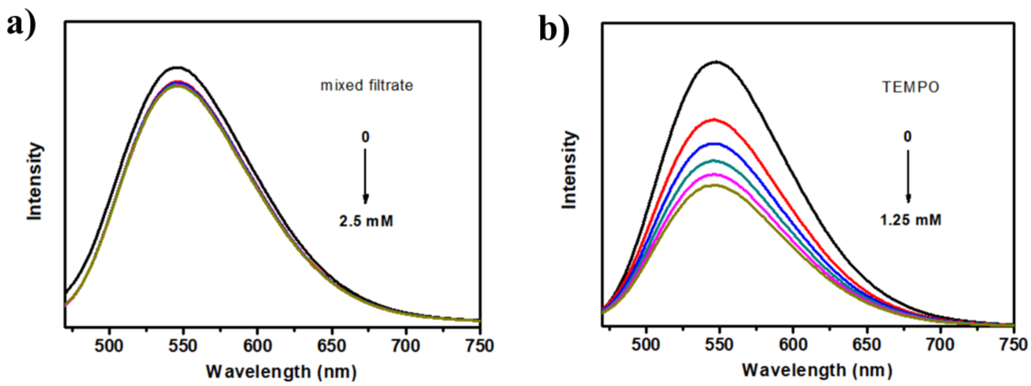


Figure S3 Luminescent quenching spectra of 4CzIPN (1×10^{-5} M) in the presence of **a)** different volume of mixed filtrate and **b)** different concentrations of TEMPO in CH_3CN with excitation at 440 nm.

3.3 The detection of H_2O_2

After the photoreaction was finished, 5 mL dichloromethane was added to the reaction mixture, and the resulting solution was filtered. Then 2 mL of saturated sodium carbonate aqueous solution was introduced into the solution to extract H_2O_2. Then, 2.5 ml of acetic acid, 2 g of NaI and 35 ml of isopropanol were injected into the H_2O_2 aqueous solution (**Figure S4**, left). After refluxing for 20 min, the solution color turned yellow (**Figure S4**, right), indicating that the H_2O_2 was generated during the reaction [4].

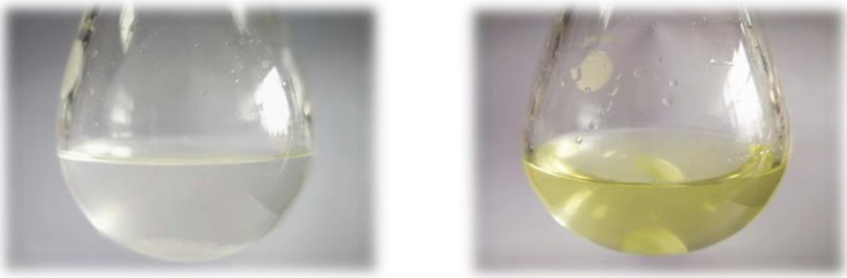


Figure S4 The detection of H_2O_2.

3.4 The Light On-off Experiments

In order to explore whether the reaction is a chain reaction or not, the light on-off experiments were carried out. Five parallel solutions were prepared with **I-1** as the template substrate under the standard condition. The solutions were alternately irradiated for 30 min and shielded from light for 30 min. The plot of the yield of **II-1** vs the reaction time was obtained below (**Figure S5**). **II-1** was only formed during periods of constant irradiation, which suggested that a chain-propagation-type mechanism was unlikely to be involved.

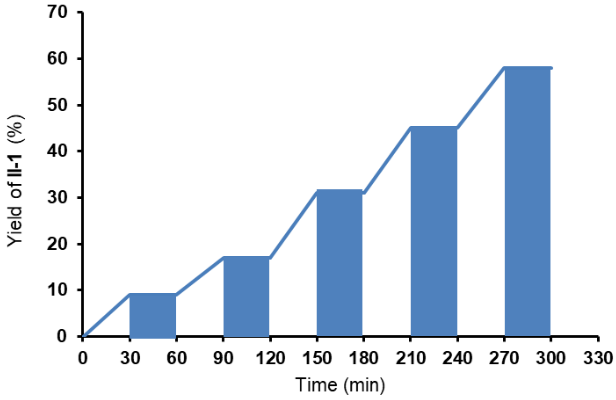
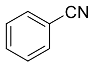


Figure S5 The light on-off experiments.

4. References

1. Lou S, Moquist PN, Schaus SE. *J. Am. Chem. Soc*, 2007, 129: 15398-15404
2. Chen GH, Brown HC. *J. Am. Chem. Soc*, 2000, 122: 4217-4218
3. Luo J, Zhang J. *ACS Catal*, 2016, 6: 873-877
4. Meng QY, Gao XW, Lei T, Liu Z, Zhan F, Li ZJ, Zhong JJ, Xiao H, Feng K, Chen B, Tao Y, Tung CH, Wu LZ. *Sci. Adv*, 2017, 3: e1700666

5. Characterization of products (II-1 ~ II-35)



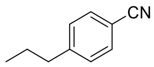
benzonitrile (II-1)

Colorless volatile liquid. Isolated yield: 33.0 mg, 80%. petroleum ether/CH_2Cl_2 = 5/1-2/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.69 – 7.41 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 132.80, 132.14, 129.15, 118.84, 112.46.

HRMS (EI): m/z calculated for C_7H_5N m/z 103.0422, found 103.0422.



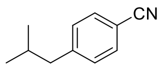
4-propylbenzonitrile (II-2)

Colorless liquid. Isolated yield: 48.2 mg, 83%. petroleum ether/CH_2Cl_2 = 5/1-2/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.54 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 7.7 Hz, 1H), 2.62 (t, J = 7.6 Hz, 2H), 1.85 – 1.46 (sex, J = 7.5 Hz, 2H), 0.92 (t, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 148.44, 132.23, 129.39, 119.23, 109.86, 38.27, 24.16, 13.75.

HRMS (EI): m/z calculated for $C_{10}H_{11}N$ m/z 145.0891, found 145.0889.



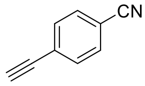
4-isobutylbenzonitrile (II-3)

Colorless liquid. Isolated yield: 55.4 mg, 87%. petroleum ether/CH_2Cl_2 = 5/1-2/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.55 (d, J = 7.9 Hz, 2H), 7.23 (d, J = 7.9 Hz, 2H), 2.53 (d, J = 7.2 Hz, 2H), 1.88 (sep, J = 6.9 Hz, 1H), 0.90 (d, J = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 147.47, 132.07, 129.97, 119.20, 109.87, 45.62, 30.13, 22.34.

HRMS (EI): m/z calculated for $C_{11}H_{13}N$ m/z 159.1048, found 159.1050.



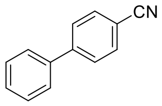
4-ethynylbenzonitrile (II-4)

White soild. Isolated yield:48.8 mg, 96%. petroleum ether/ CH_2Cl_2=5/1-2/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.55 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 8.0 Hz, 1H), 3.23 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 132.81, 132.16, 127.14, 118.37, 112.49, 82.00, 81.67.

HRMS (EI): m/z calculated for C_9H_5N m/z 127.0422, found 127.0418.



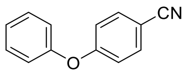
[1,1'-biphenyl]-4-carbonitrile (II-5)

White soild. Isolated yield: 60.4 mg, 83%. petroleum ether/ CH_2Cl_2=5/1-2/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.72 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 7.9 Hz, 2H), 7.54 – 7.40 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 145.67, 139.18, 132.61, 129.16, 128.71, 127.75, 127.25, 118.96, 110.96.

HRMS (EI): m/z calculated for $C_{13}H_9N$ m/z 179.0735, found 179.0725.



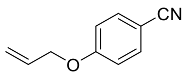
4-phenoxybenzonitrile (II-6)

Colorless oil. Isolated yield: 73.6mg, 93%. petroleum ether/ CH_2Cl_2=5/1-1/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.60 (d, J = 8.6 Hz, 2H), 7.41 (t, J = 7.8 Hz, 2H), 7.23 (t, J = 7.4 Hz, 1H), 7.07 (d, J = 8.2 Hz, 2H), 7.00 (d, J = 8.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 161.77, 154.95, 134.24, 130.34, 125.25, 120.51, 118.93, 118.05, 105.97.

HRMS (EI): m/z calculated for $C_{13}H_9NO$ m/z 195.0684, found 195.0680.



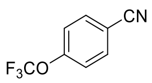
4-(allyloxy)benzonitrile (II-7)

White soild. Isolated yield: 41.4 mg, 65%. petroleum ether/ CH_2Cl_2=5/1-2/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.57 (d, J = 8.6 Hz, 2H), 6.95 (d, J = 8.6 Hz, 2H), 6.02 (m, 1H), 5.41 (d, J = 17.3 Hz, 1H), 5.33 (d, J = 10.5 Hz, 1H), 4.58 (d, J = 5.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 161.97, 134.07, 132.21, 119.26, 118.57, 115.59, 104.25, 69.13.

HRMS (EI): m/z calculated for $C_{10}H_9NO$ m/z159.0684, found 159.0679.



4-(trifluoromethoxy)benzonitrile (II-8)

Colorless liquid. Isolated yield: 48.6 mg, 65%. petroleum ether/ CH_2Cl_2=5/1-1/1.

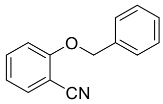
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.73 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 152.36 (d, J = 1.8 Hz), 134.32, 121.37 (d, J = 0.9 Hz), 124.19 –

116.45 (q, J = 133.42 Hz), 117.77, 111.00.

^{19}F NMR (377 MHz, $CDCl_3$, ppm) *δ:* -57.74.

HRMS (EI): m/z calculated for $C_8H_4F_3NO$ m/z 187.0245., found187.0240.



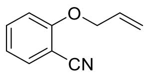
2-(benzyloxy)benzonitrile (II-9)

White soild. Isolated yield: 66.9 mg, 80%. petroleum ether/ CH_2Cl_2=5/1-2/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) *δ*: 7.57 (d, *J* = 7.7 Hz, 1H), 7.48 (m, 3H), 7.36 (m, 3H), 7.01 (m, 2H), 5.21 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) *δ*: 160.47, 135.85, 134.30, 133.94, 128.81, 128.30, 127.10, 121.21, 116.43, 113.21, 102.78, 70.84.

HRMS (EI): m/z calculated for $C_{14}H_{11}NO$ m/z 209.0841, found 209.0837.



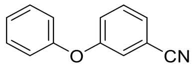
2-(allyloxy)benzonitrile ((II-10)

Colorless liquid. Isolated yield: 57.3mg, 90%. petroleum ether/ CH_2Cl_2=5/1-1/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) *δ*: 7.72 – 7.36 (m, 2H), 7.18 – 6.62 (m, 2H), 6.04 (m, 1H), 5.47 (d, *J* = 17.3 Hz, 1H), 5.32 (d, *J* = 10.6 Hz, 1H), 4.66 (d, *J* = 4.9 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) *δ*: 160.33, 134.31, 133.87, 131.98, 120.99, 118.32, 116.50, 112.76, 102.35, 69.55.

HRMS (EI): m/z calculated for $C_{10}H_9NO$ m/z159.0684, found 159.0679.



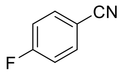
3-phenoxybenzonitrile (II-11)

Pale yellow liquid. Isolated yield: 67.9mg, 87%. petroleum ether/ CH_2Cl_2=5/1-1/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) *δ*: 7.39 (m, 7.1 Hz, 4H), 7.28 – 7.16 (m, 3H), 7.04 (d, J = 8.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) *δ*: 158.31, 155.66, 130.77, 130.30, 126.51, 124.82, 122.88, 121.20, 119.88, 118.36, 113.68.

HRMS (EI): m/z calculated for $C_{13}H_9NO$ m/z 195.0684, found 195.0680.



4-fluorobenzonitrile (II-12)

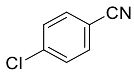
Colorless volatile liquid. Isolated yield: 29 mg, 60%. petroleum ether/ CH_2Cl_2=5/1-2/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.68 (dd, J = 8.0, 5.4 Hz, 2H), 7.18 (t, J = 8.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 165.15 (d, J = 256.5 Hz), 134.78 (d, J = 9.3 Hz), 118.10, 116.95 (d, J = 22.7 Hz), 108.70 (d, J = 3.7 Hz).

^{19}F NMR (377 MHz, $CDCl_3$, ppm) δ: -102.45.

HRMS (EI): m/z calculated for C_7H_4FN m/z 121.0328, found 121.0323.



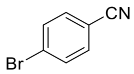
4-chlorobenzonitrile (II-13)

White solid. Isolated yield: 47.9 mg, 87%. petroleum ether/ CH_2Cl_2=5/1-2/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.60 (d, J = 8.3 Hz, 2H), 7.46 (d, J = 8.3 Hz, 2H).

^{13}C NMR (400 MHz, $CDCl_3$, ppm) δ: 139.68, 133.50, 129.82, 118.07, 110.95.

HRMS (EI): m/z calculated for C_7H_4ClN m/z 137.0032, found 137.0031.



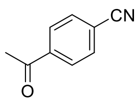
4-bromobenzonitrile (II-14)

White solid. Isolated yield: 56.1 mg, 77%. petroleum ether/ CH_2Cl_2=5/1-2/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.63 (d, J = 8.3 Hz, 2H), 7.52 (d, J = 8.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 133.49, 132.73, 128.09, 118.12, 111.36.

HRMS (EI): m/z calculated for C_7H_4BrN m/z 180.9527, found 180.9525.



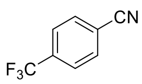
4-acetylbenzonitrile (II-15)

White solid. Isolated yield: 38.3 mg, 66%. petroleum ether/ EtOAc =10/1-5/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.04 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H), 2.64 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 196.63, 140.09, 132.66, 128.83, 118.04, 116.59, 26.88.

HRMS (EI): m/z calculated for C_9H_7NO m/z 145.0528, found 145.0527.



4-(trifluoromethyl)benzonitrile (II-16)

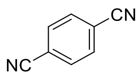
Colorless liquid. Isolated yield: 47.2 mg, 69%. petroleum ether/ CH_2Cl_2=5/1-1/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.81 (d, J = 8.3 Hz, 2H), 7.76 (d, J = 8.3 Hz, 2H).

^{13}C NMR (101 MHz, CDCl3, ppm) δ: 134.75 (q, J = 33.4 Hz), 132.83, 126.34 (q, J = 3.7 Hz), 127.27 – 119.13 (q, J = 273.9 Hz), 117.55, 116.27.

^{19}F NMR (377 MHz, $CDCl_3$, ppm) δ: -63.54.

HRMS (EI): m/z calculated for $C_8H_4F_3N$ m/z 171.0296, found 171.0289.



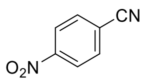
terephthalonitrile (II-17)

White solid. Isolated yield: 38.4 mg, 75%, petroleum ether/EtOAc = 10/1-5/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.79 (s, 4H).

^{13}C NMR (400 MHz, $CDCl_3$, ppm) δ: 132.93, 117.12, 116.90.

HRMS (EI): m/z calculated for $C_8H_4N_2$ m/z 128.0374, found 128.0372.



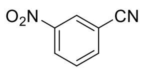
4-nitrobenzonitrile (II-18)

White solid. Isolated yield: 37.2 mg, 63%. petroleum ether/EtOAc=10/1-5/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.35 (d, J = 8.5 Hz, 2H), 7.89 (d, J = 8.5 Hz, 1H).

^{13}C NMR (400 MHz, $CDCl_3$, ppm) δ: 150.18, 133.59, 124.41, 118.47, 116.90.

HRMS (EI): m/z calculated for $C_7H_4N_2O_2$ m/z 148.0273, found 148.0270.

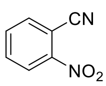


3-nitrobenzonitrile (II-19)

White solid. Isolated yield: 46.8 mg, 79%. petroleum ether/EtOAc = 10/1-5/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.54 (s, 1H), 8.48 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 7.7 Hz, 1H), 7.74 (t, J = 8.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 148.40, 137.70, 130.78, 127.65, 127.36, 116.64, 114.32.



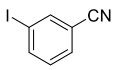
2-nitrobenzonitrile (II-20)

Yellow solid. Isolated yield: 35.0 mg, 59%. petroleum ether/ CH_2Cl_2/EtOAc = 3:2:0.5

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.38 – 8.29 (m, 1H), 7.96 – 7.90 (m, 1H), 7.90 – 7.78 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 148.72, 135.72, 134.42, 133.82, 125.68, 115.03, 108.24.

HRMS (EI): m/z calculated for $C_7H_4N_2O_2$ m/z 148.0273, found 148.0274.



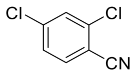
3-iodobenzonitrile (II-21)

Colorless liquid. Isolated yield: 76.0 mg, 83%. petroleum ether/ CH_2Cl_2=5/1-1/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.88 (s, 1H), 7.85 (d, J = 8.1 Hz, 1H), 7.54 (d, J = 7.6 Hz, 1H), 7.13 (t, J = 7.9 Hz, 1H)..

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 141.95, 140.46, 131.25, 130.61, 117.13, 114.28, 93.94.

HRMS (EI): m/z calculated for C_7H_4IN m/z 228.9388, found 228.9385.



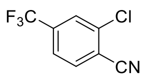
2,4-dichlorobenzonitrile (II-22)

White solid. Isolated yield: 51.6 mg, 75%. petroleum ether/ CH_2Cl_2=5/1-1/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.61 (d, J = 8.4 Hz, 1H), 7.54 (s, 1H), 7.37 (d, J = 8.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 140.22, 137.98, 134.70, 130.41, 127.98, 115.2, 112.14.

HRMS (EI): m/z calculated for $C_7H_3Cl_2N$ m/z 170.9643, found 170.9645.



2-chloro-4-(trifluoromethyl)benzonitrile (II-23)

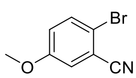
Colorless liquid. Isolated yield: 45.2 mg, 55%. petroleum ether/ CH_2Cl_2=5/1-1/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.99 (s, 1H), 7.78 (d, J = 8.3 Hz, 1H), 7.67 (d, J = 8.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 138.00, 135.90 (q, J = 34.0 Hz), 134.74, 127.30 (q, J = 3.8 Hz), 124.25 (q, J = 3.6 Hz), 126.54 – 118.38 (q, J = 274.52 Hz), 117.13, 114.83.

^{19}F NMR (377 MHz, $CDCl_3$, ppm) δ: -63.61.

HRMS (EI): m/z calculated for $C_8H_3ClF_3N$ m/z 204.9906, found 204.9900.



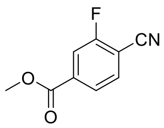
2-bromo-5-methoxybenzonitrile (II-24)

Crystal solid. Isolated yield: 67.8 mg, 80%. petroleum ether/ CH_2Cl_2=5/1-1/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.52 (d, J = 9.0 Hz, 1H), 7.13 (d, J = 3.0 Hz, 1H), 6.99 (dd, J = 9.0, 3.0 Hz, 1H), 3.81 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 158.82, 134.09, 120.92, 119.03, 117.16, 116.34, 115.68, 55.99.

HRMS (EI): m/z calculated for C_8H_6BrNO m/z 210.9633, found 210.9630.



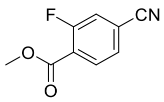
methyl 4-cyano-3-fluorobenzoate (II-25)

White solid. Isolated yield: 53.7 mg, 75%. petroleum ether/ EtOAc =10/1-5/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.93 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 9.2 Hz, 1H), 7.72 (t, J = 7.0 Hz, 1H), 3.97 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 164.48 (d, J = 2.5 Hz), 163.03 (d, J = 260.4 Hz), 136.67 (d, J = 7.6 Hz), 133.82, 125.76 (d, J = 3.8 Hz), 117.58 (d, J = 21.4 Hz), 113.26, 105.69 (d, J = 15.7 Hz), 53.16.

HRMS (EI): m/z calculated for $C_9H_6FNO_2$ m/z 179.0383, found 179.0380.



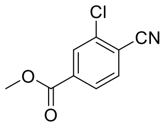
methyl 4-cyano-2-fluorobenzoate (II-26)

White solid. Isolated yield: 55.9 mg, 78%. petroleum ether/ EtOAc =10/1-5/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.04 (t, J = 7.4 Hz, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.45 (d, J = 9.7 Hz, 1H), 3.96 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 163.44 (d, J = 3.8 Hz), 161.26 (d, J = 263.8 Hz), 133.24 (d, J = 1.4 Hz), 127.82 (d, J = 4.5 Hz), 123.20 (d, J = 10.5 Hz), 121.00 (d, J = 26.1 Hz), 117.69 (d, J = 9.7 Hz), 116.70 (d, J = 2.5 Hz), 53.03.

HRMS (EI): m/z calculated for $C_9H_6FNO_2$ m/z 179.0383, found 179.0380.



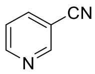
methyl 3-chloro-4-cyanobenzoate (II-27)

White solid. Isolated yield: 47.7 mg, 61%. petroleum ether/ EtOAc =10/1-5/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.16 (s, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 3.96 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 164.51, 137.36, 135.34, 133.18, 130.97, 128.05, 117.28, 115.36, 53.14.

HRMS (EI): m/z calculated for $C_9H_6ClNO_2$ m/z 195.0087, found 195.0085.



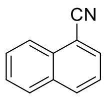
nicotinonitrile (II-28)

Pale yellow solid. Isolated yield: 34.6 mg, 83%. petroleum ether/ EtOAc=2/1-1/1.

H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.83 (s, 1H), 8.76 (d, J = 4.7 Hz, 1H), 7.93 (d, J = 7.9 Hz, 1H), 7.47 – 7.33 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 152.95, 152.39, 139.21, 123.60, 116.46, 110.04.

HRMS (EI): m/z calculated for $C_6H_4N_2$ m/z 104.0374, found 104.0373.



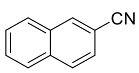
1-naphthonitrile (II-29)

Colorless liquid. Isolated yield: 49.2 mg, 79%. petroleum ether/ CH_2Cl_2=5/1-2/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.25 (d, J = 8.3 Hz, 1H), 8.09 (d, J = 8.3 Hz, 1H), 7.93 (dd, J = 7.6, 4.5 Hz, 2H), 7.71 (t, J = 7.6 Hz, 1H), 7.63 (t, J = 7.5 Hz, 1H), 7.53 (t, J = 7.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 133.41, 133.10, 132.77, 132.54, 128.79, 128.75, 127.70, 125.33, 125.07, 117.94, 110.40.

HRMS (EI): m/z calculated for $C_{11}H_7N$ m/z 153.0578, found 153.0580.



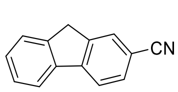
2-naphthonitrile (II-30)

White soild. Isolated yield: 36.8 mg, 60%. petroleum ether/ CH2Cl2=5/1-2/1.

1H NMR (400 MHz, CDCl3, ppm) δ: 8.22 (s, 1H), 7.90 (t, J = 8.5 Hz, 3H), 7.62 (m, 3H).

13C NMR (101 MHz, CDCl3, ppm) δ: 134.82, 134.24, 132.46, 129.31, 129.14, 128.53, 128.18, 127.77, 126.48, 119.28, 109.64.

HRMS (EI): m/z calculated for $C_{11}H_7N$ m/z 153.0578, found 153.0580.White soild. Isolated yield:



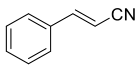
9*H*-fluorene-2-carbonitrile (II-31)

White soild. Isolated yield: 67.3 mg, 88%. petroleum ether/ CH_2Cl_2=5/1-2/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.81 (d, J = 7.8 Hz, 2H), 7.78 (s, 1H), 7.65 (d, J = 7.9 Hz, 1H), 7.59 (d, J = 6.8 Hz, 1H), 7.42 (m, 2H), 3.91 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 146.32, 144.02, 143.76, 140.03, 131.25, 128.69, 127.41, 125.40, 121.05, 120.45, 119.66, 109.89, 36.87.

HRMS (EI): m/z calculated for $C_{14}H_9N$ m/z 191.0735, found 191.0736.



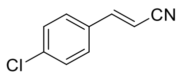
cinnamonitrile (II-32)

Colorless volatile liquid. Isolated yield: 17.1 mg, 33%. petroleum ether/ CH_2Cl_2=5/1-1/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.41 – 7.31 (m, 5H), 7.28 (d, J = 16.7 Hz, 1H), 5.79 (d, J = 16.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 150.27, 133.33, 131.00, 128.91, 127.21, 118.03, 96.15.

HRMS (EI): m/z calculated for C_9H_7N m/z 129.0578, found 129.0574.



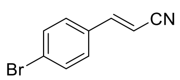
(*E*)-3-(4-chlorophenyl)acrylonitrile (II-33)

Colorless volatile liquid. Isolated yield: 20.9 mg, 32%. petroleum ether/ CH_2Cl_2=5/1-1/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.75 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 12.1 Hz, 1H), 5.48 (d, J = 12.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 147.41, 137.15, 132.14, 130.40, 129.40, 117.18, 95.86.

HRMS (EI): m/z calculated for C_9H_6ClN m/z 163.0189, found 163.0189.



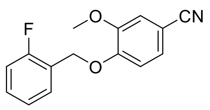
(*E*)-3-(4-bromophenyl)acrylonitrile (II-34)

White solid. Isolated yield: 29.1 mg, 35%. petroleum ether/ CH_2Cl_2=5/1-1/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.67 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 7.8 Hz, 2H), 7.07 (d, J = 12.1 Hz, 1H), 5.49 (d, J = 12.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 147.46, 132.42, 130.51, 125.51, 117.12, 95.99.

HRMS (EI): m/z calculated for C_9H_6BrN m/z 206.9684, found 206.9680.



4-((2-fluorobenzyl)oxy)-3-methoxybenzonitrile (II-35)

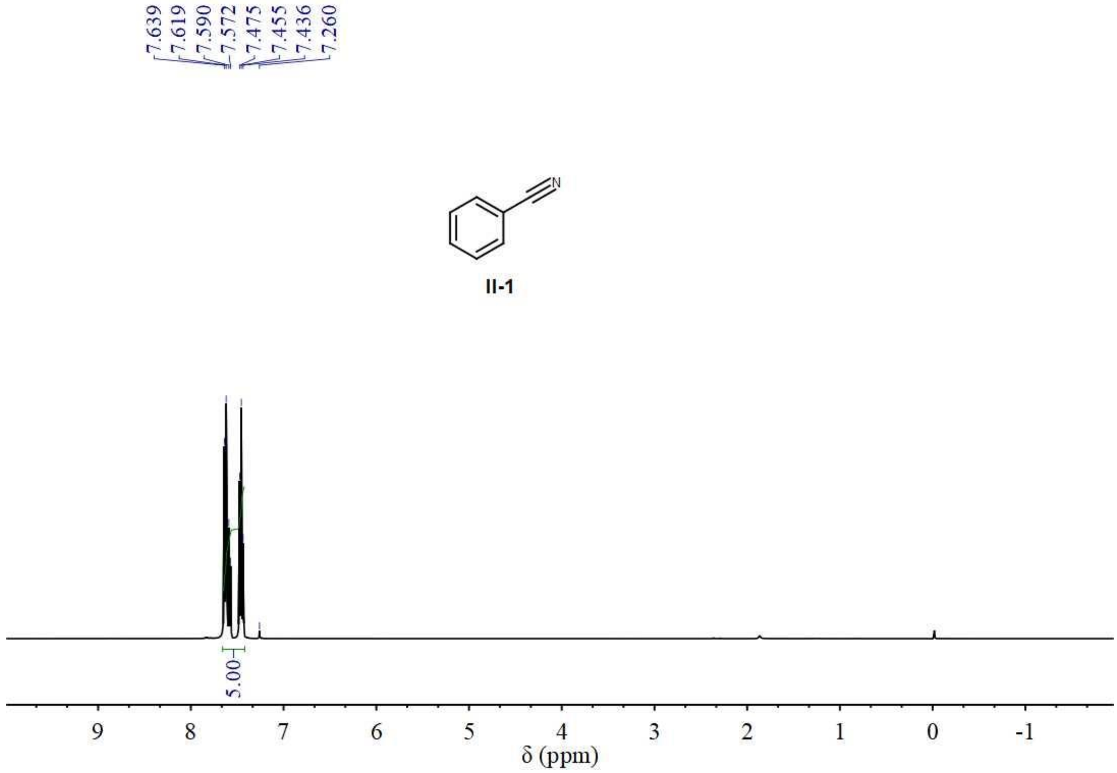
White solid. Isolated yield: 84.3 mg, 82%. petroleum ether/ EtOAc=10/1-5/1.

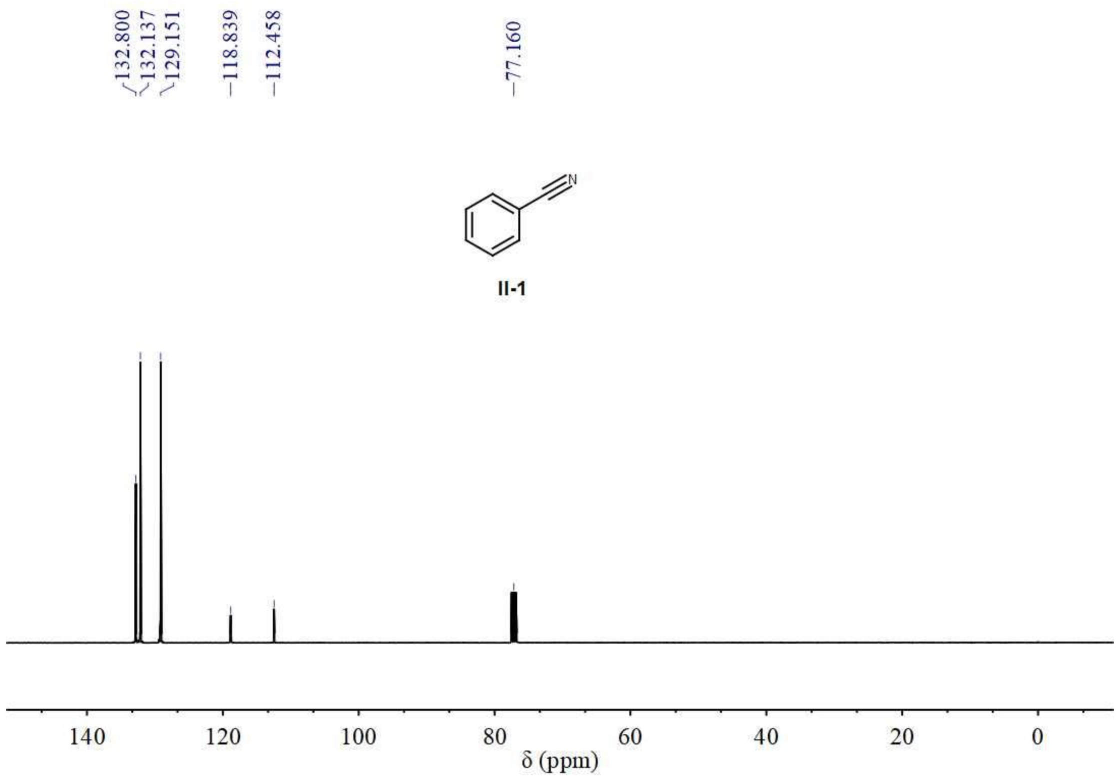
H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.41 (t, J = 7.3 Hz, 1H), 7.29 – 6.97 (m, 5H), 6.88 (d, J = 8.3 Hz, 1H), 5.18 (s, 2H), 3.82 (s, 3H).

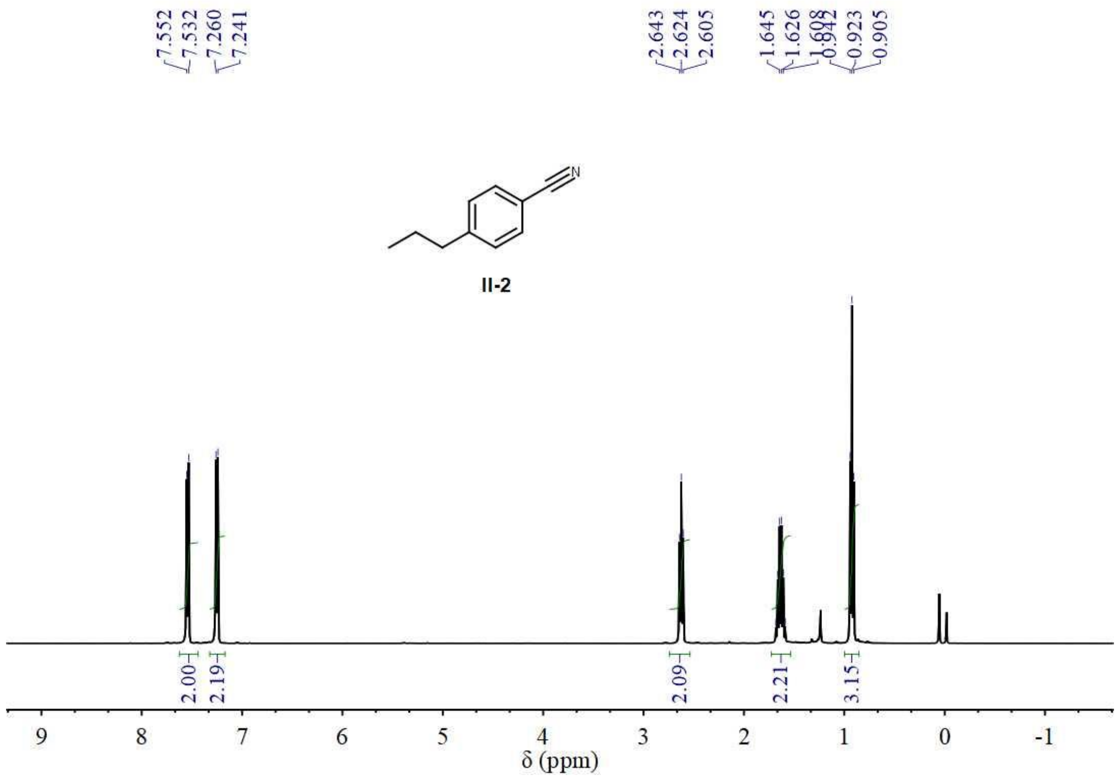
^{13}C NMR (101 MHz, CDCl3, ppm) δ: 160.50 (d, J = 247.1 Hz), 151.91, 149.93, 130.24 (d, J = 8.2 Hz), 129.71 (d, J = 3.7 Hz), 126.40, 124.57 (d, J = 3.6 Hz), 123.16 (d, J = 14.1 Hz), 119.22, 115.59 (d, J = 21.1 Hz), 114.74, 113.50, 104.71, 64.75 (d, J = 4.5 Hz), 56.35.

HRMS (EI): m/z calculated for $C_{15}H_{12}FNO_2$ m/z 257.0852, found 257.0848.

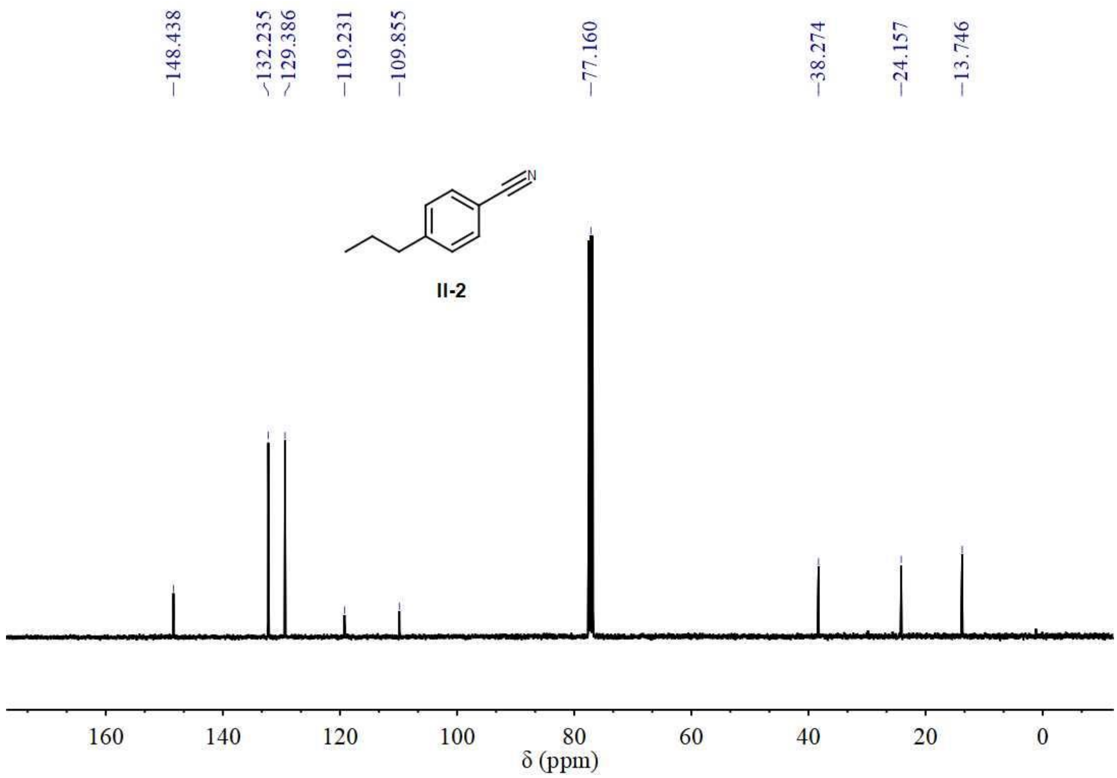
6. NMR Spectra



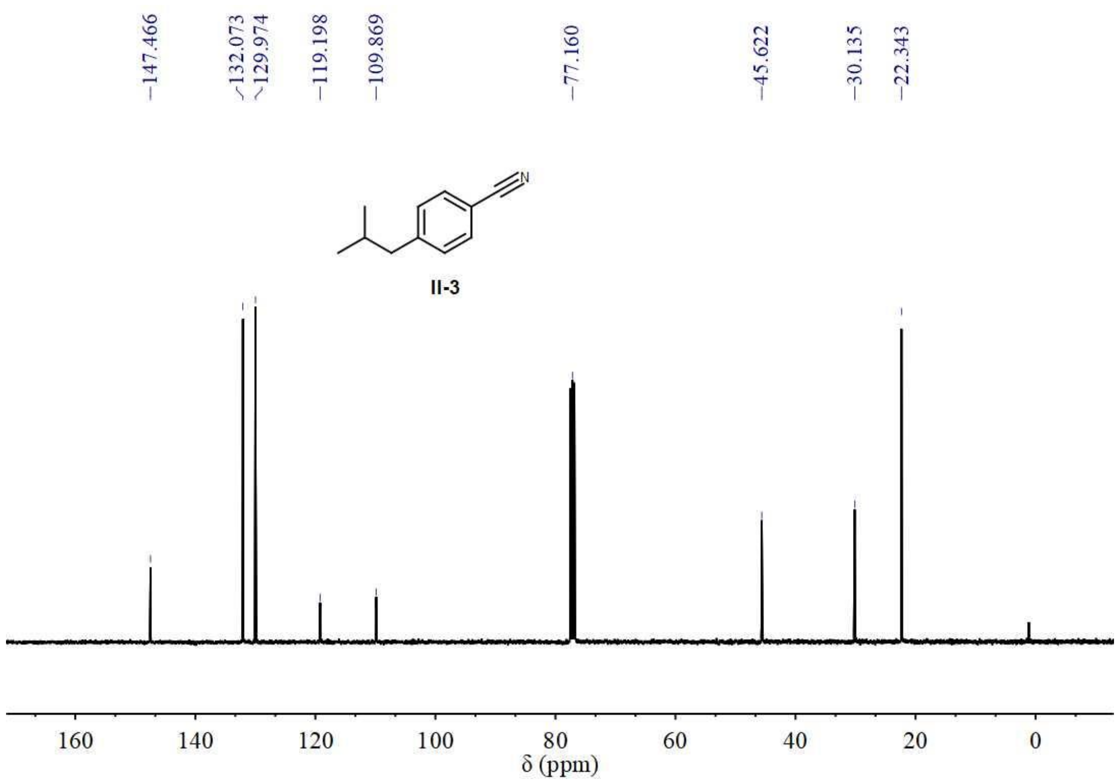




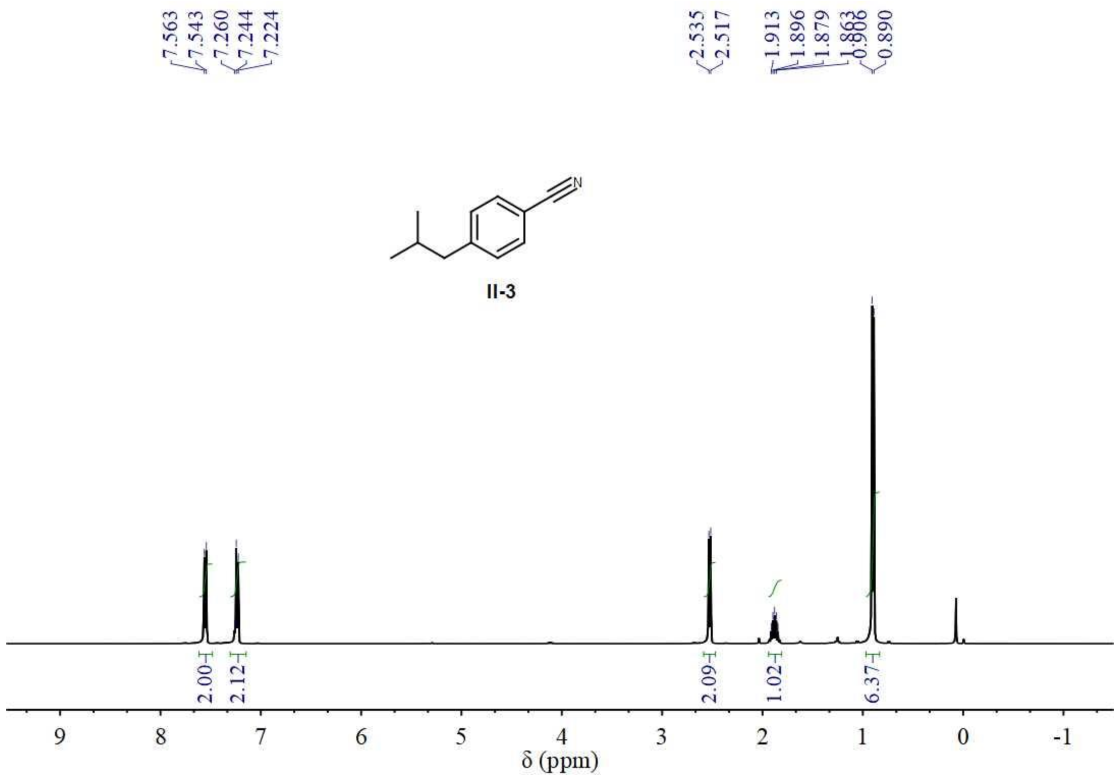
7.552
7.532
7.260
7.241
2.643
2.624
2.605
1.645
1.626
1.608
0.942
0.923
0.905
N
II-2
2.00
2.19
2.09
2.21
3.15
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)



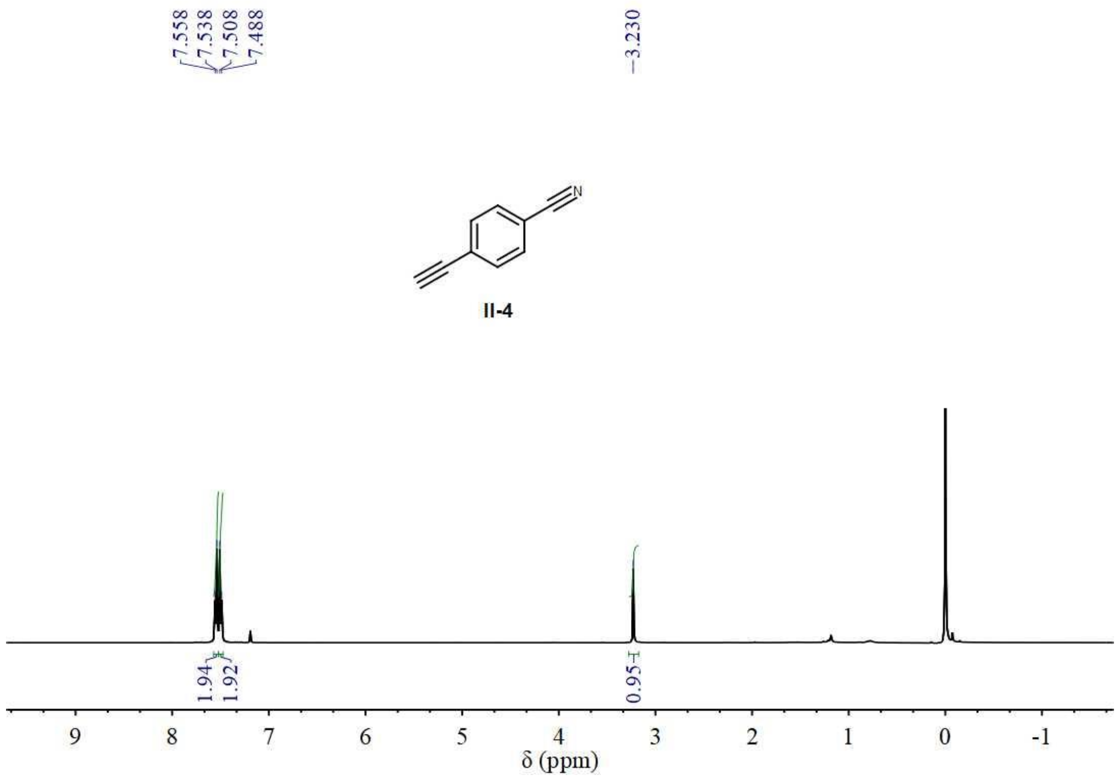
148.438
132.235
129.386
119.231
109.855
77.160
38.274
24.157
13.746
N
II-2
160
140
120
100
80
60
40
20
0
δ (ppm)

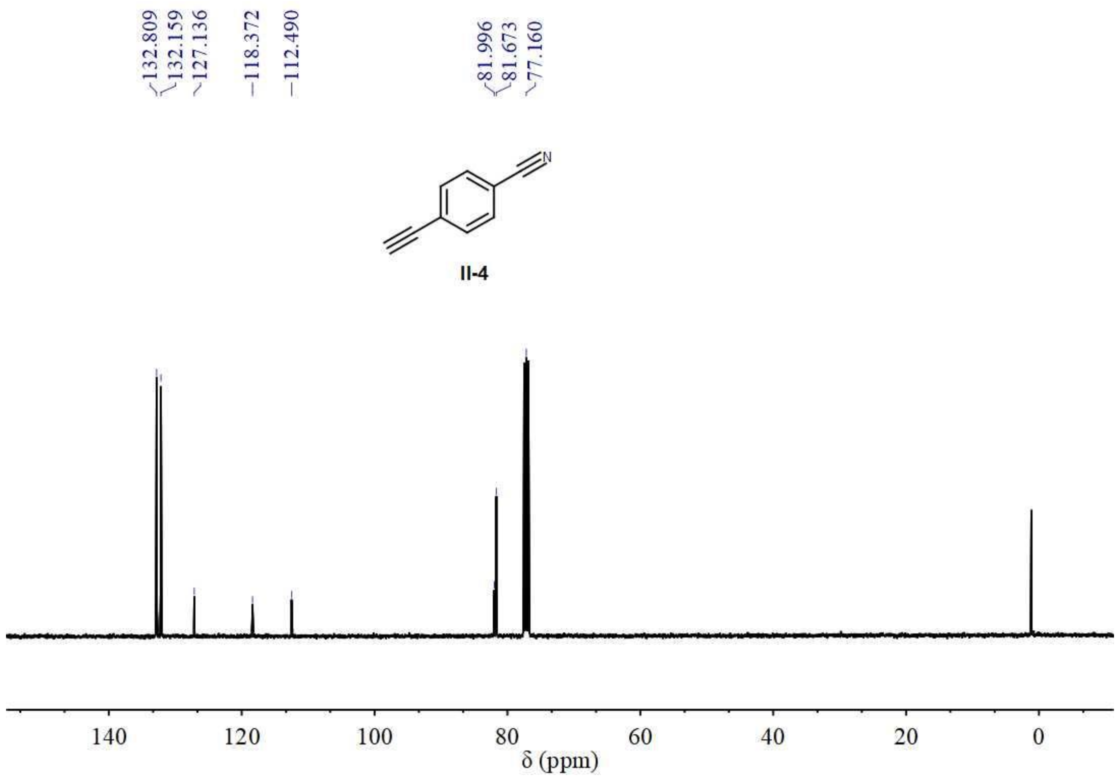


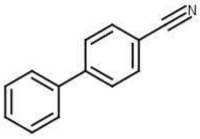
147.466
132.073
129.974
119.198
109.869
77.160
45.622
30.135
22.343
II-3
160
140
120
100
80
60
40
20
0
δ (ppm)



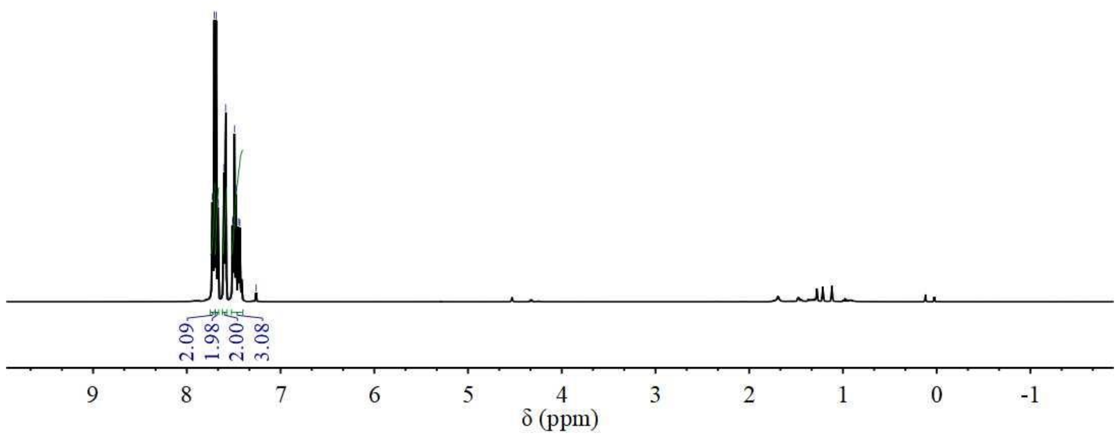
7.563
7.543
7.260
7.244
7.224
2.535
2.517
1.913
1.896
1.879
1.863
0.906
0.890
II-3
2.00
2.12
2.09
1.02
6.37
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

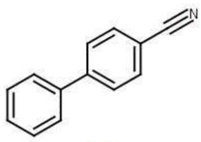

7.558
7.538
7.508
7.488
3.230
N
II-4
1.94
1.92
0.95
9 8 7 6 5 4 3 2 1 0 -1
δ (ppm)


132.809
132.159
127.136
118.372
112.490
81.996
81.673
77.160
N
II-4
140 120 100 80 60 40 20 0
δ (ppm)

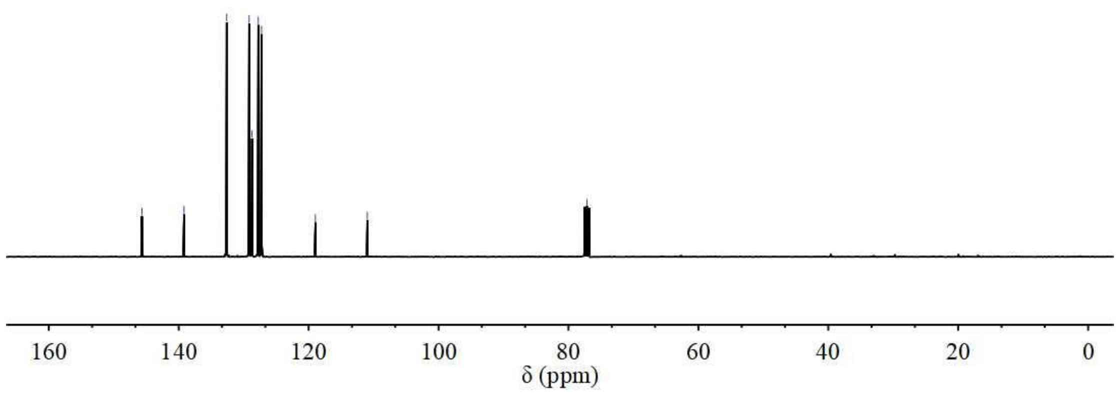

N

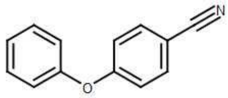
II-5


7.727
7.706
7.687
7.666
7.604
7.584
7.511
7.492
7.473
7.450
7.433
7.260
2.09
1.98
2.00
3.08
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

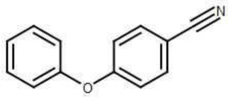

N

II-5

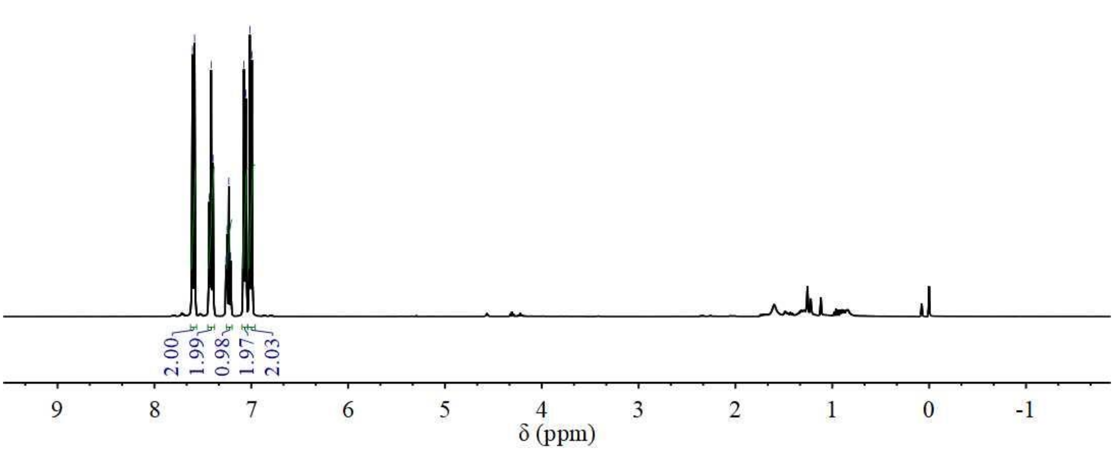

145.670
139.178
132.611
129.155
128.712
127.746
127.252
118.958
110.960
77.160
160
140
120
100
80
60
40
20
0
δ (ppm)

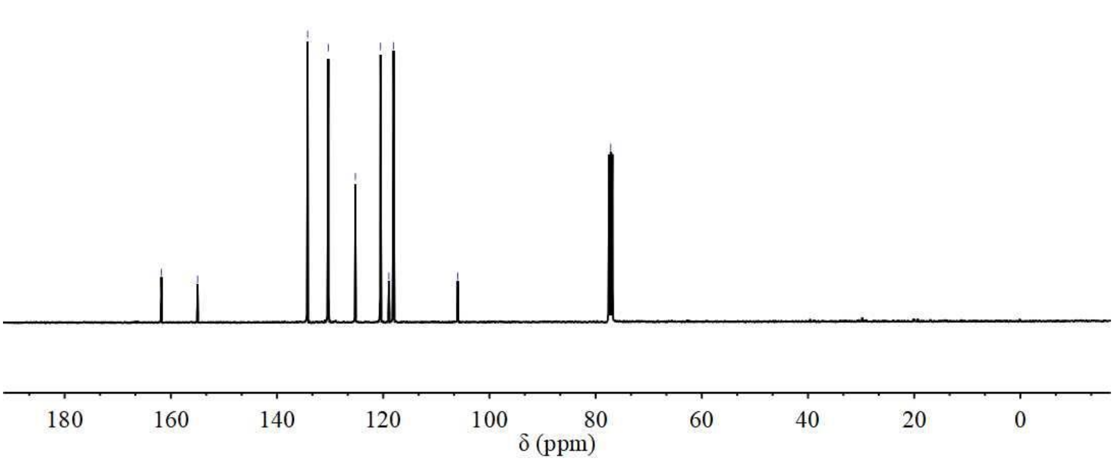


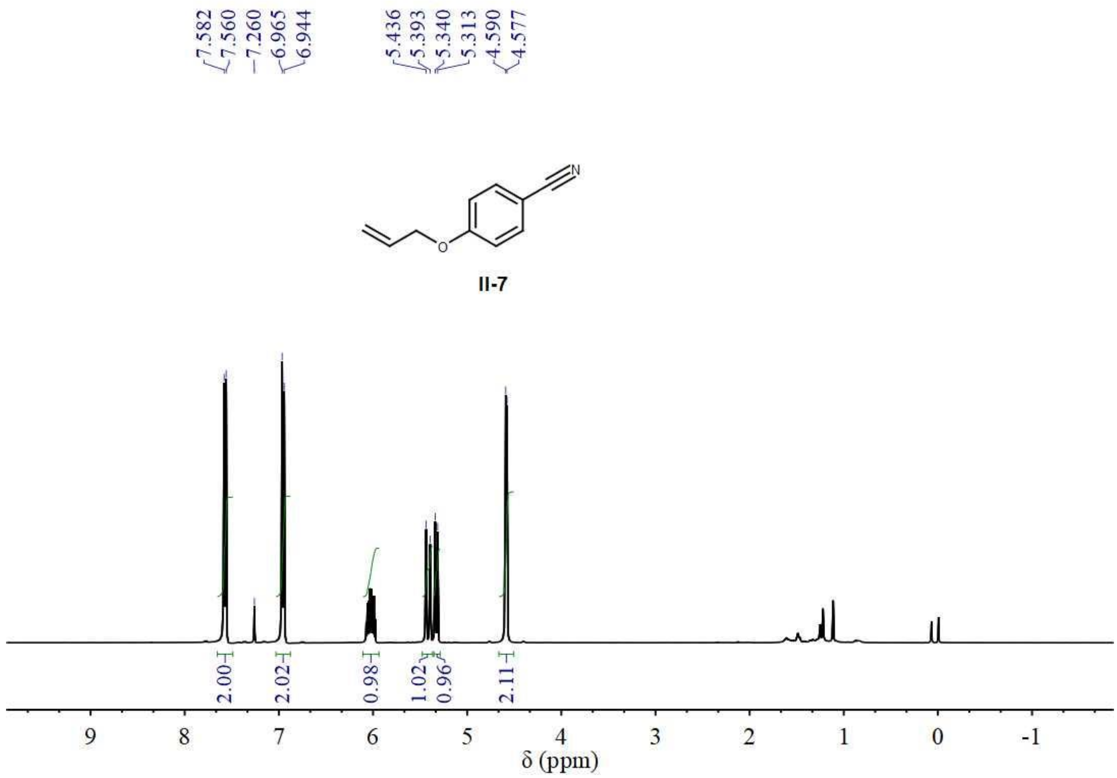
II-6

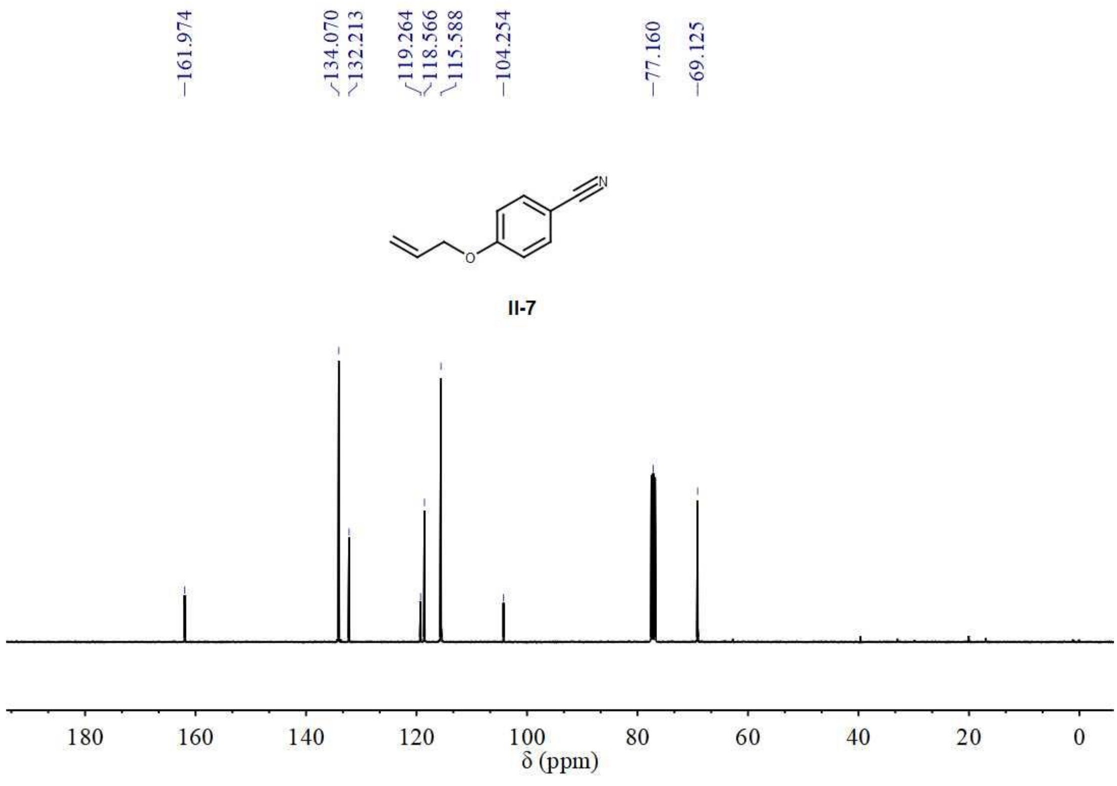


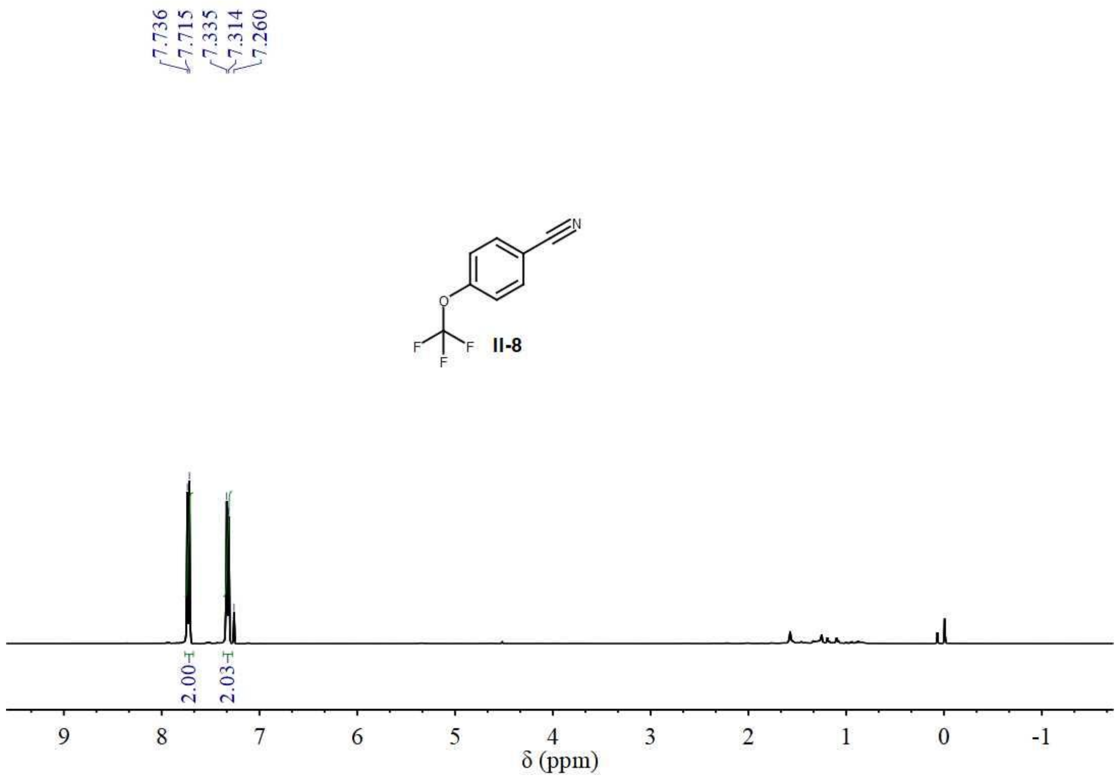
II-6

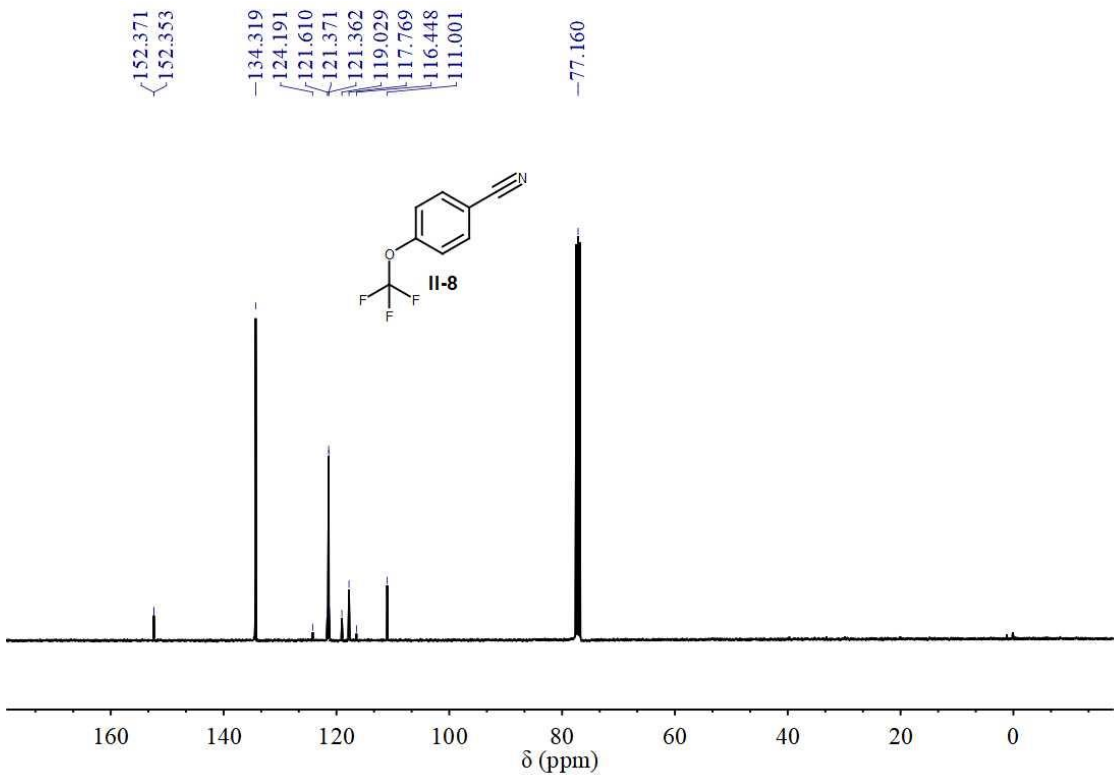


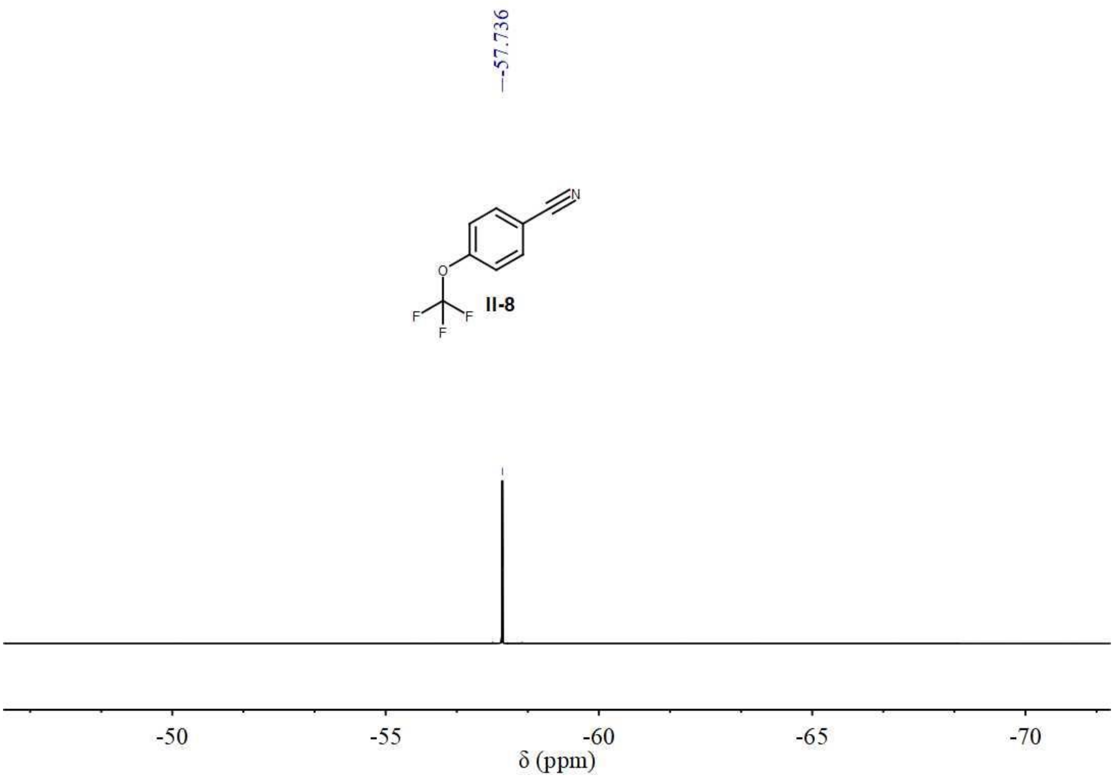


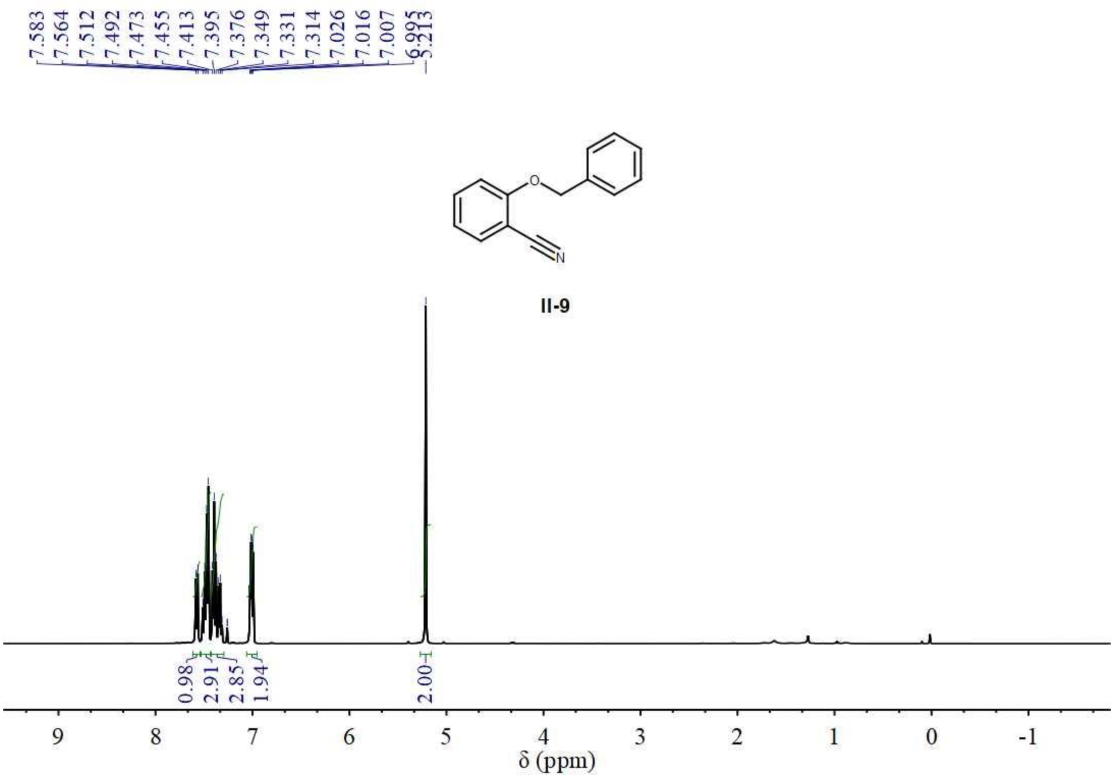

7.582
7.560
7.260
6.965
6.944
5.436
5.393
5.340
5.313
4.590
4.577
N
O
II-7
2.00
2.02
0.98
1.02
0.96
2.11
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

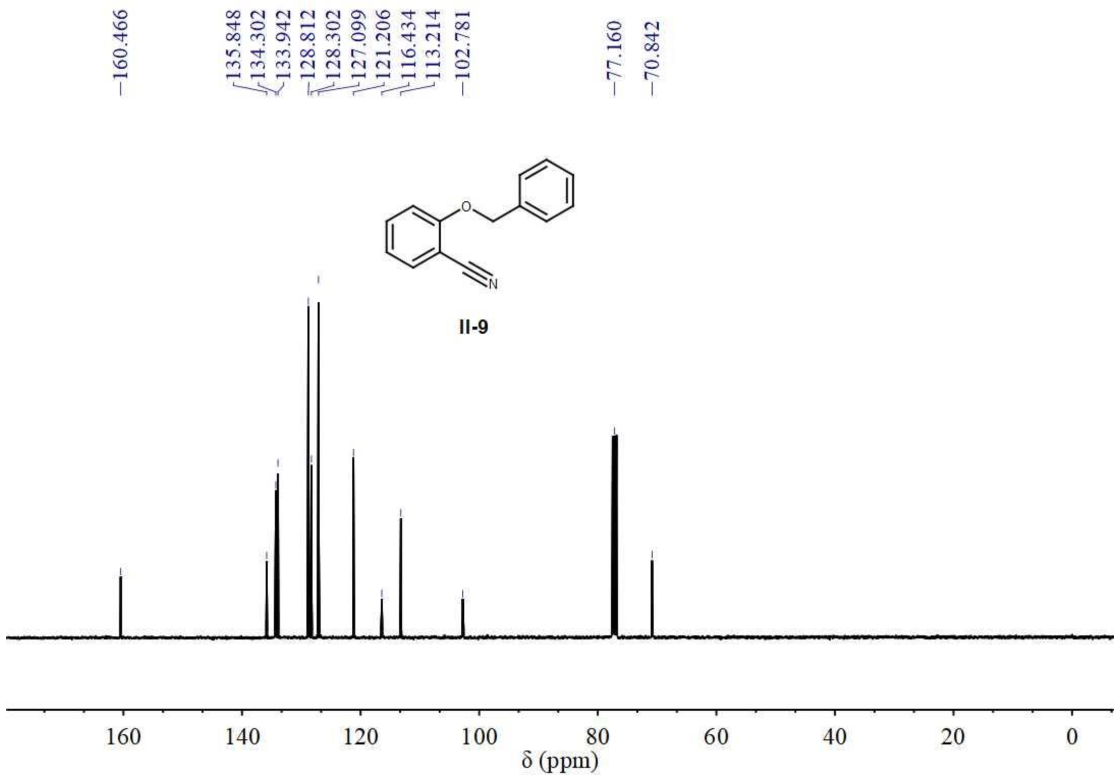

161.974
134.070
132.213
119.264
118.566
115.588
104.254
77.160
69.125
N
O
II-7
180
160
140
120
100
80
60
40
20
0
δ (ppm)

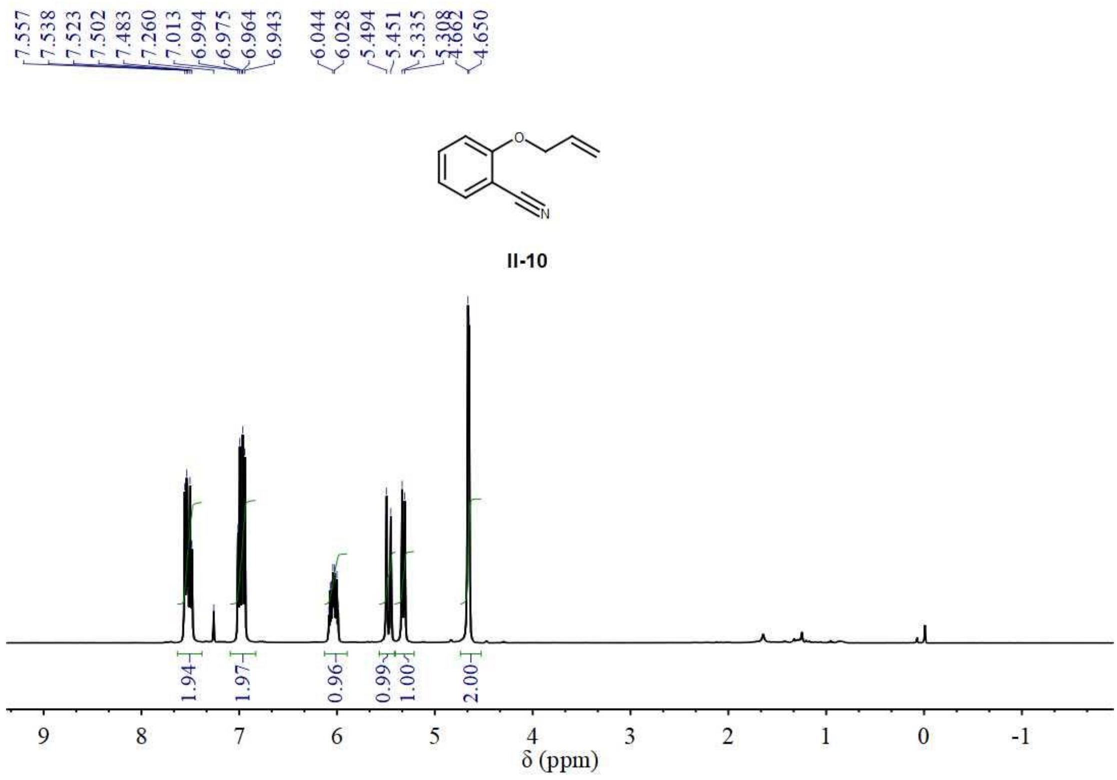

7.736
7.715
7.335
7.314
7.260
N
O
F
F
F
II-8
2.00
2.03
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

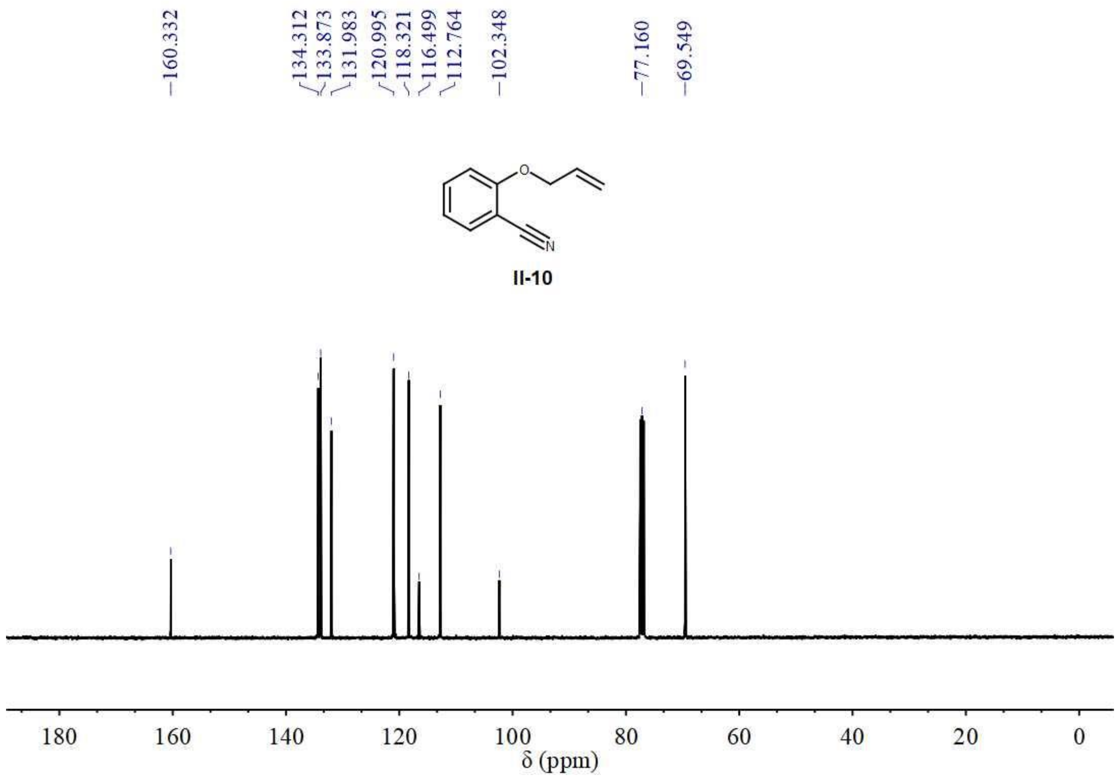

152.371
152.353
134.319
124.191
121.610
121.371
121.362
119.029
117.769
116.448
111.001
77.160
N
O
F
F
F
II-8
160
140
120
100
80
60
40
20
0
δ (ppm)


-57.736
II-8
-50
-55
-60
-65
-70
δ (ppm)

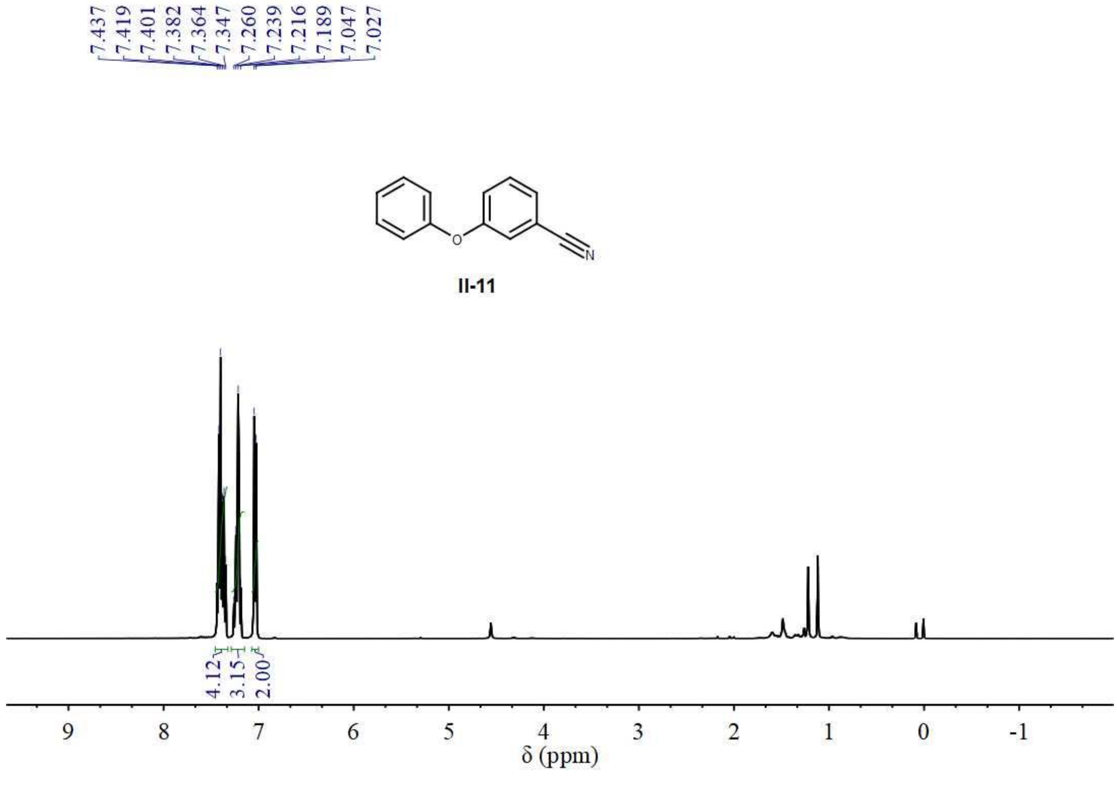

7.583
7.564
7.512
7.492
7.473
7.455
7.413
7.395
7.376
7.349
7.331
7.314
7.026
7.016
7.007
6.995
5.213
II-9
0.98
2.91
2.85
1.94
2.00
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)


160.466
135.848
134.302
133.942
128.812
128.302
127.099
121.206
116.434
113.214
102.781
77.160
70.842
O
N
II-9
160
140
120
100
80
60
40
20
0
δ (ppm)

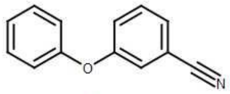

7.557
7.538
7.523
7.502
7.483
7.260
7.013
6.994
6.975
6.964
6.943
6.044
6.028
5.494
5.451
5.335
5.308
4.662
4.650
O
N
II-10
1.94
1.97
0.96
0.99
1.00
2.00
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)



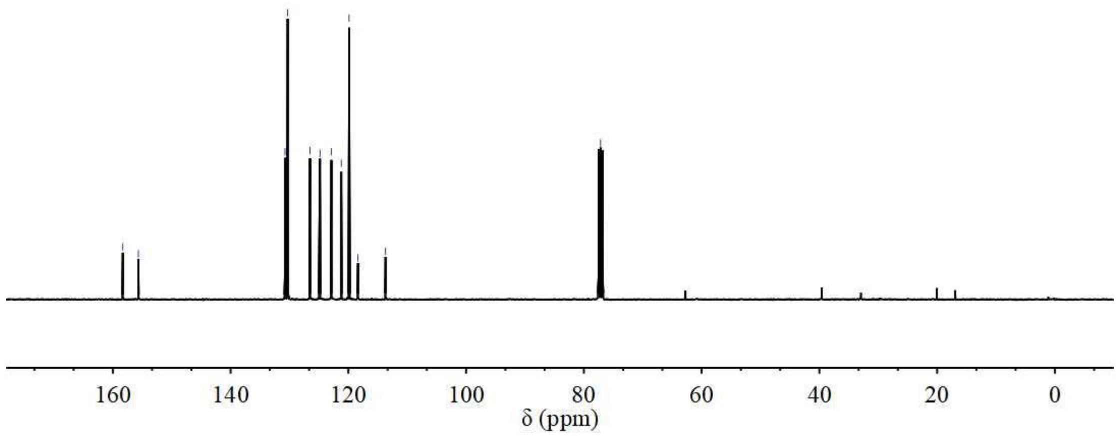
160.332
134.312
133.873
131.983
120.995
118.321
116.499
112.764
102.348
77.160
69.549
O
N
II-10
180
160
140
120
100
80
60
40
20
0
δ (ppm)

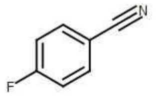


7.437
7.419
7.401
7.382
7.364
7.347
7.260
7.239
7.216
7.189
7.047
7.027
O
N
II-11
4.12
3.15
2.00
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

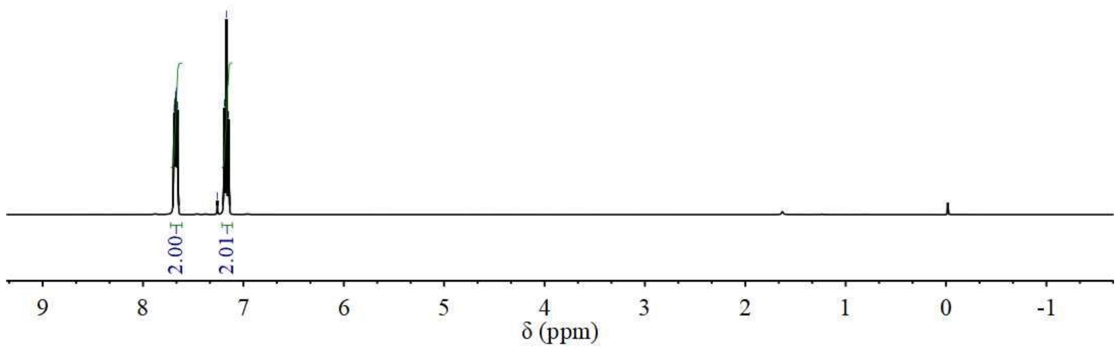


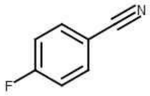
II-11


158.306
155.659
130.771
130.301
126.510
124.820
122.876
121.198
119.883
118.362
113.682
77.160
160
140
120
100
80
60
40
20
0
δ (ppm)

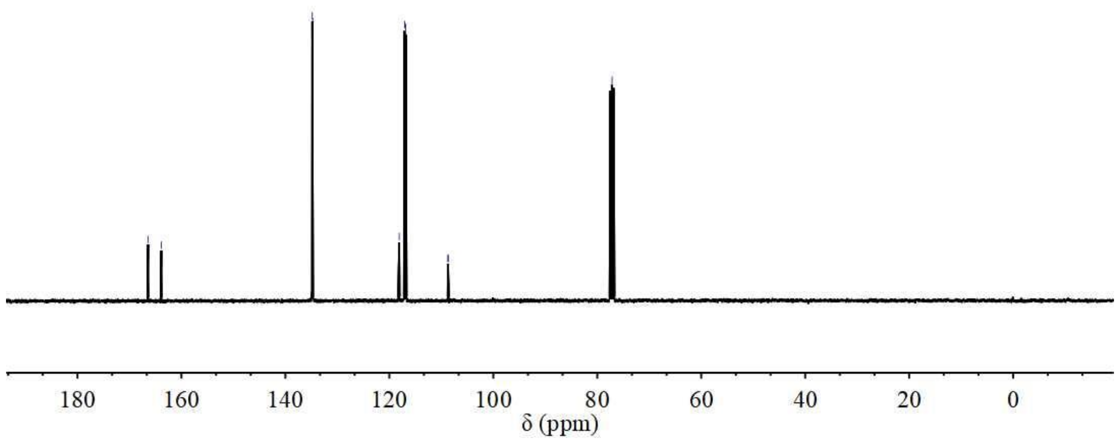


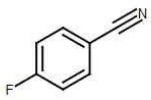
II-12


7.690
7.676
7.669
7.656
7.260
7.190
7.169
7.148
2.00
2.01
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

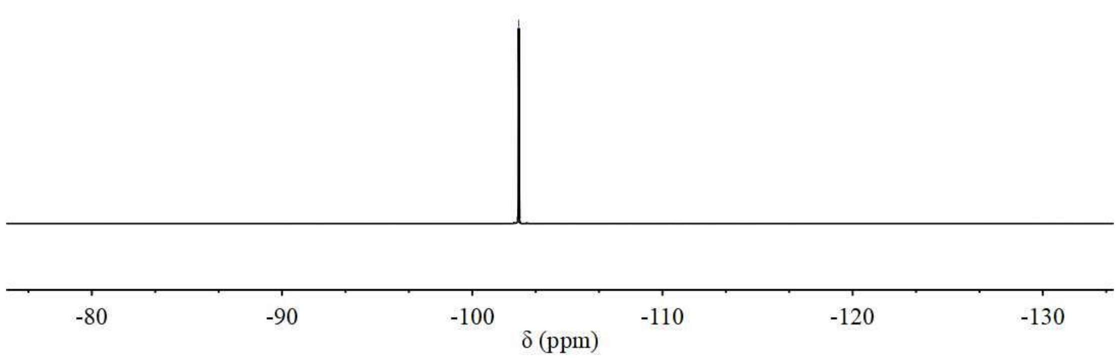


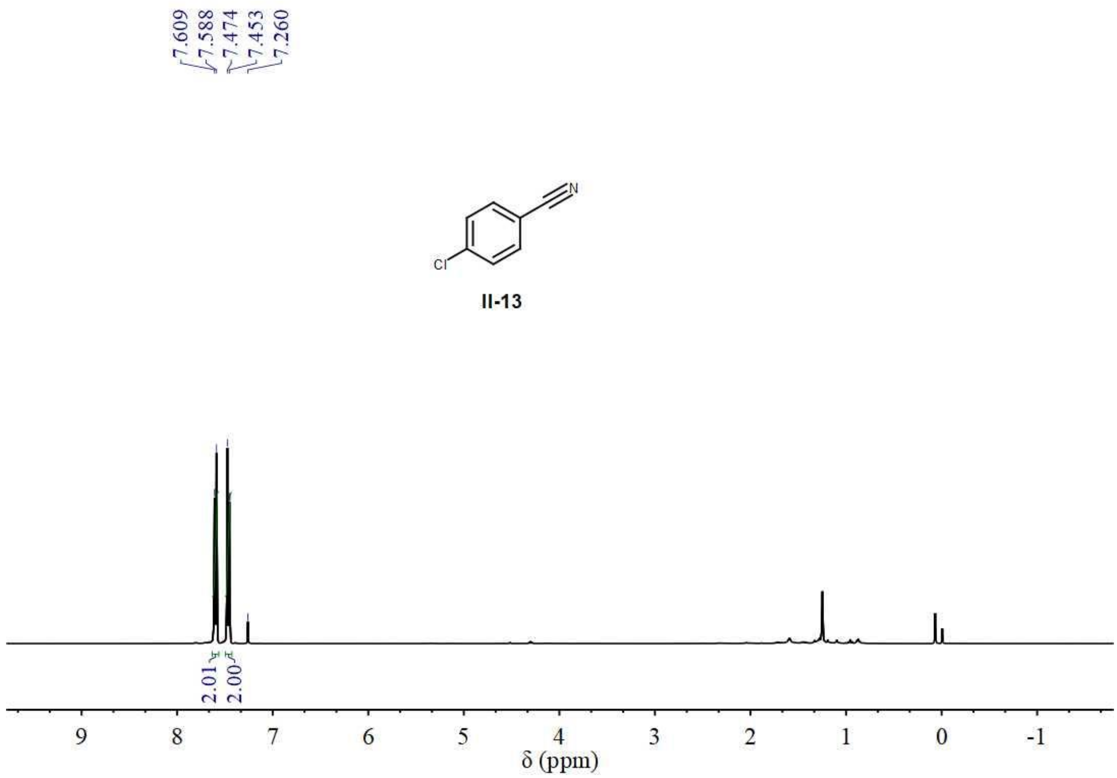
II-12

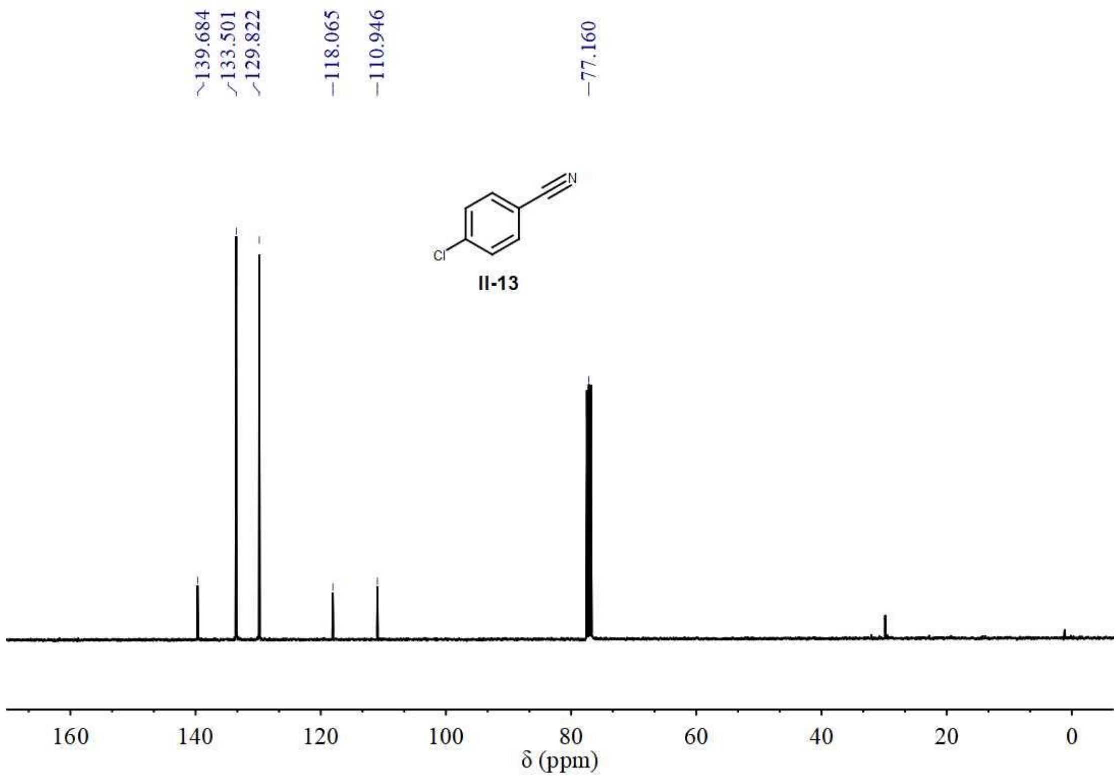

166.420
163.871
134.830
134.737
118.103
117.067
116.841
108.721
108.685
77.160
180 160 140 120 100 80 60 40 20 0
δ (ppm)

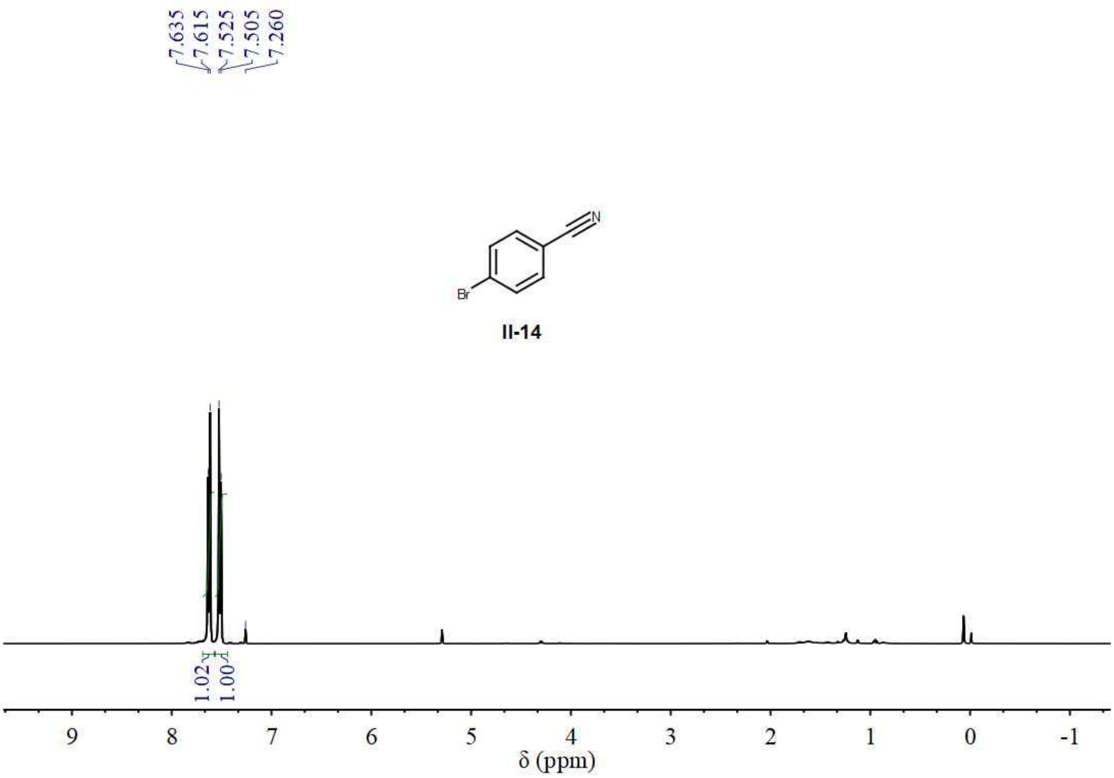


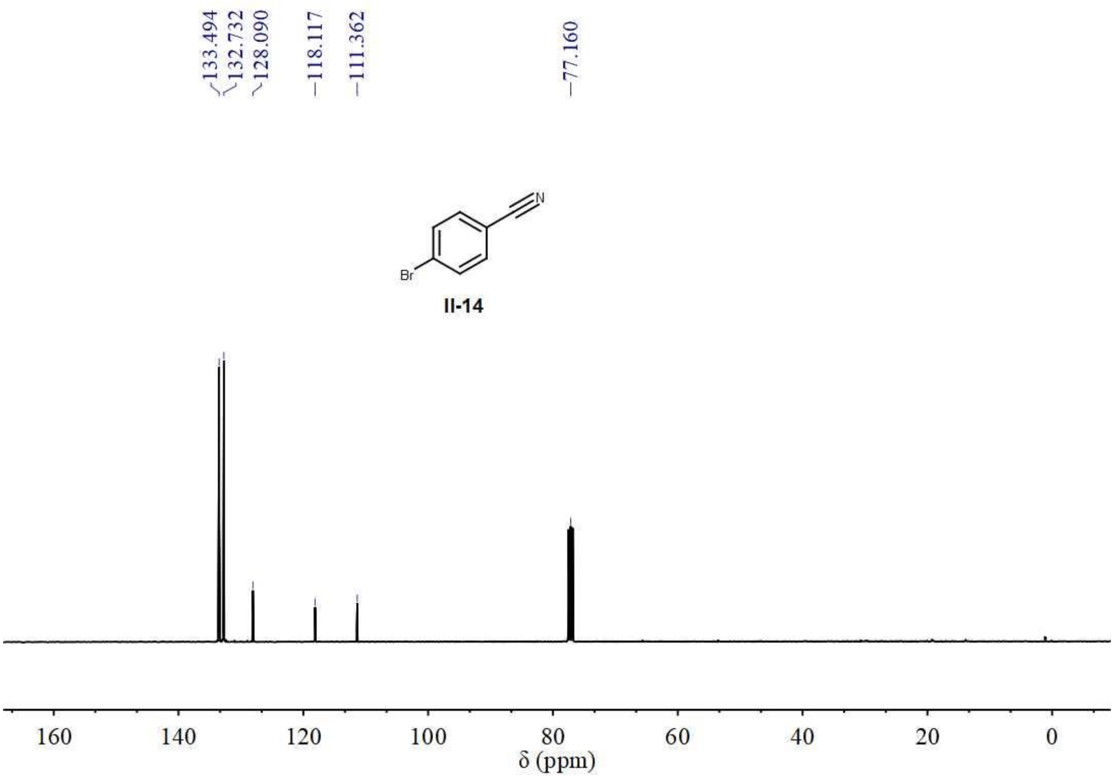
II-12

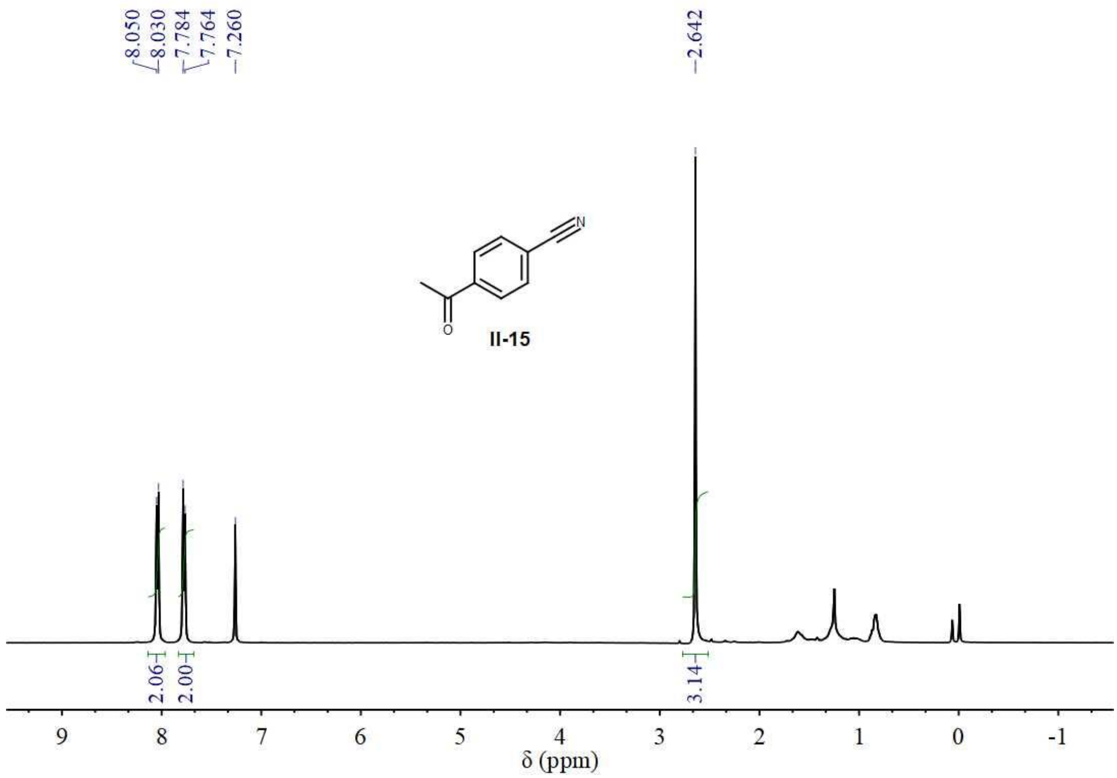

-102.446
-80 -90 -100 -110 -120 -130
δ (ppm)

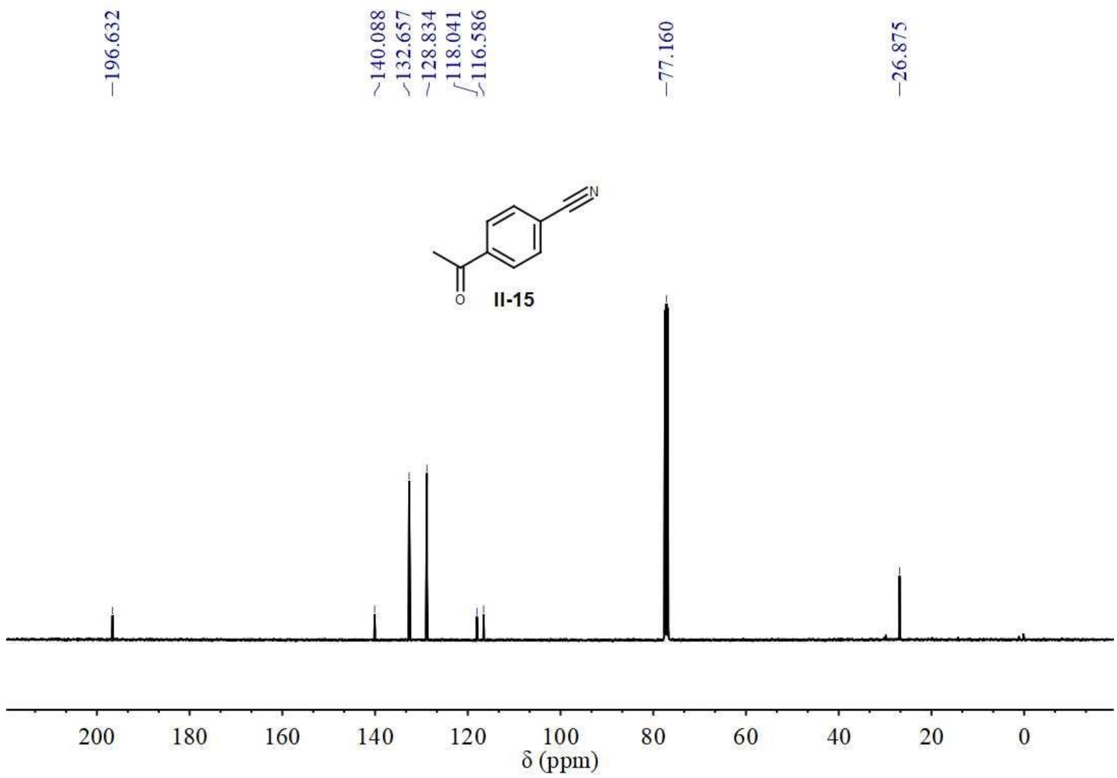

7.609
7.588
7.474
7.453
7.260
Cl
N
II-13
2.01
2.00
9 8 7 6 5 4 3 2 1 0 -1
δ (ppm)

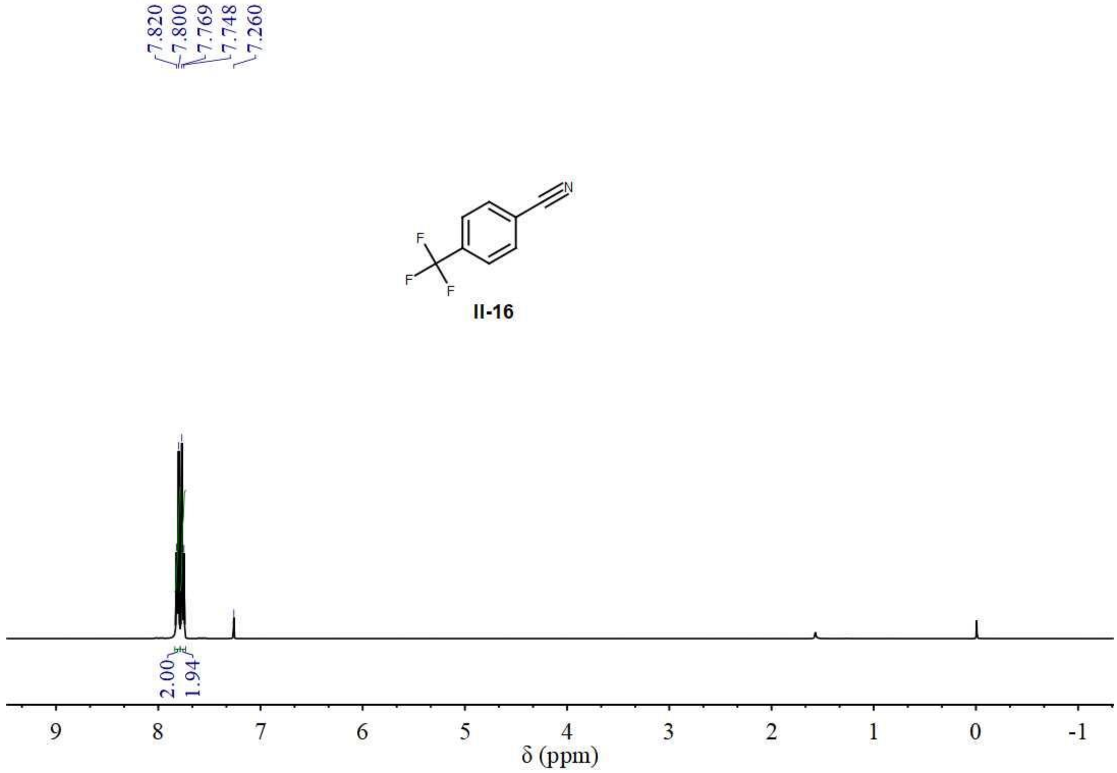

139.684
133.501
129.822
118.065
110.946
77.160
Cl
N
II-13
160 140 120 100 80 60 40 20 0
δ (ppm)

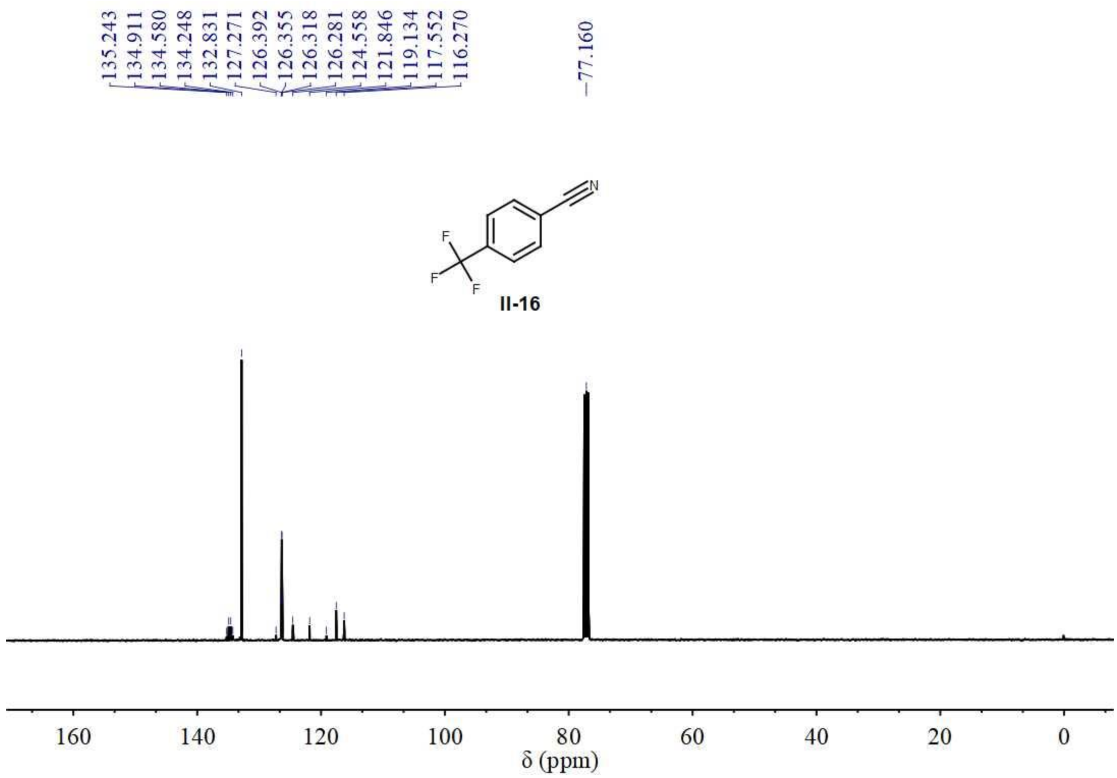

7.635
7.615
7.525
7.505
7.260
Br
N
II-14
1.02
1.00
9 8 7 6 5 4 3 2 1 0 -1
δ (ppm)

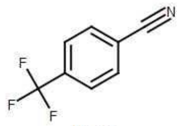

133.494
132.732
128.090
118.117
111.362
77.160
Br
N
II-14
160 140 120 100 80 60 40 20 0
δ (ppm)


8.050
8.030
7.784
7.764
7.260
2.642
N
O
II-15
2.06
2.00
3.14
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

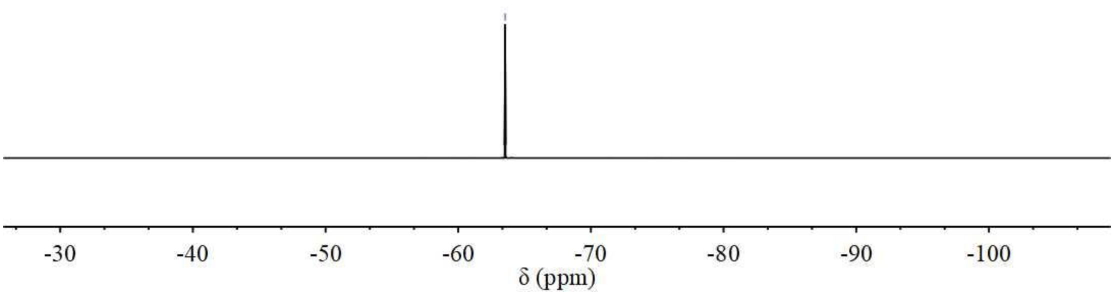

196.632
140.088
132.657
128.834
118.041
116.586
77.160
26.875
N
O
II-15
200
180
160
140
120
100
80
60
40
20
0
δ (ppm)


7.820
7.800
7.769
7.748
7.260
II-16
2.00
1.94
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

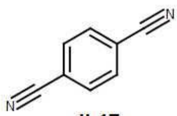

135.243
134.911
134.580
134.248
132.831
127.271
126.392
126.355
126.318
126.281
124.558
121.846
119.134
117.552
116.270
77.160
II-16
160
140
120
100
80
60
40
20
0
δ (ppm)



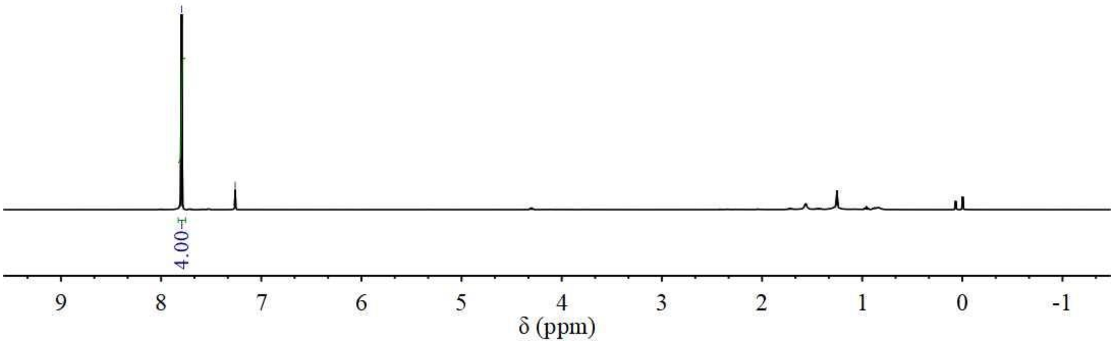
II-16



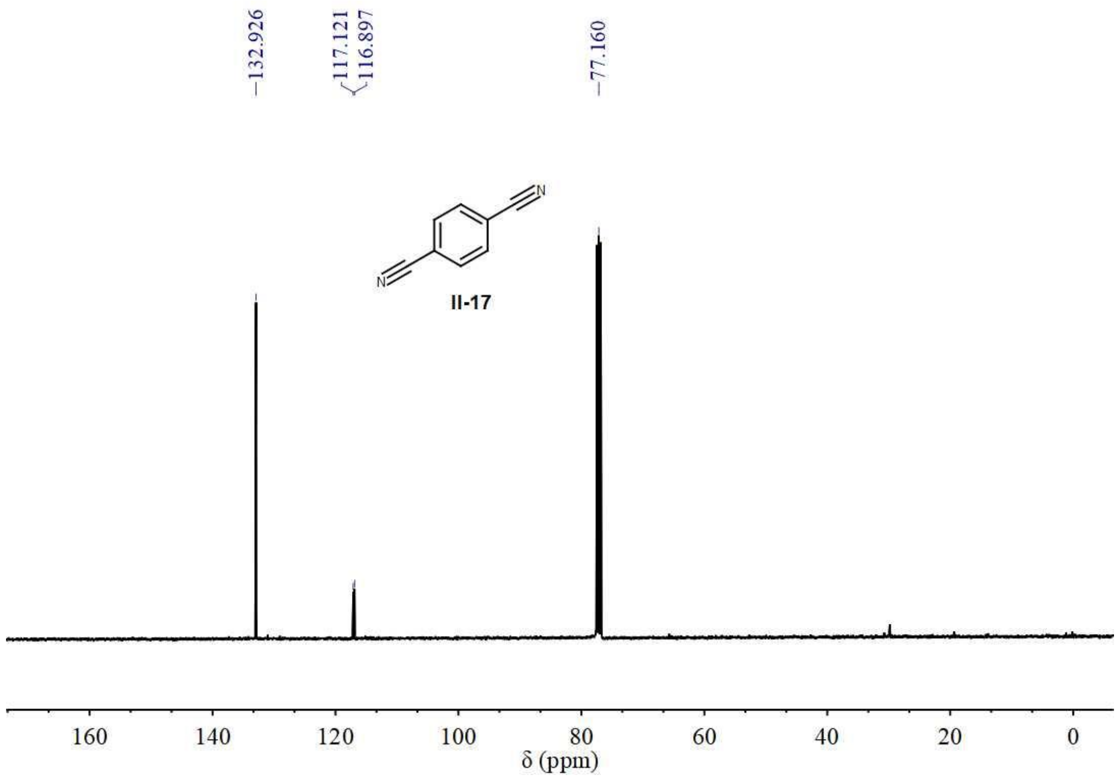
-63.537
-30
-40
-50
-60
-70
-80
-90
-100
δ (ppm)



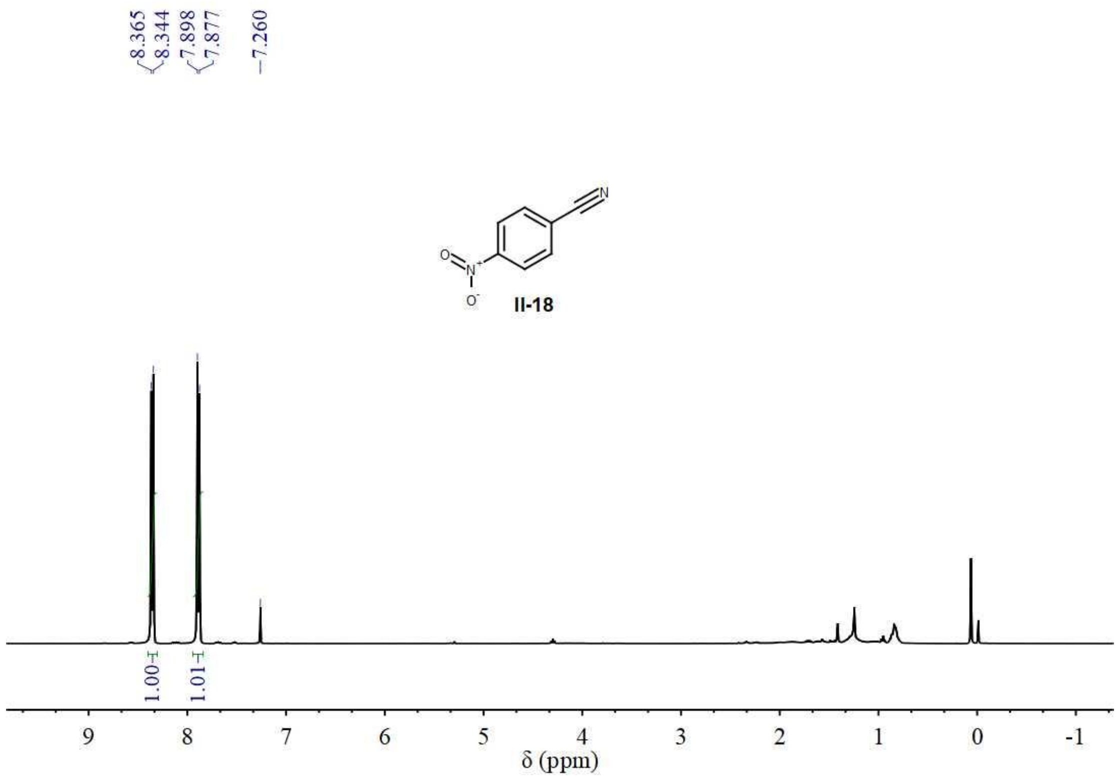
II-17



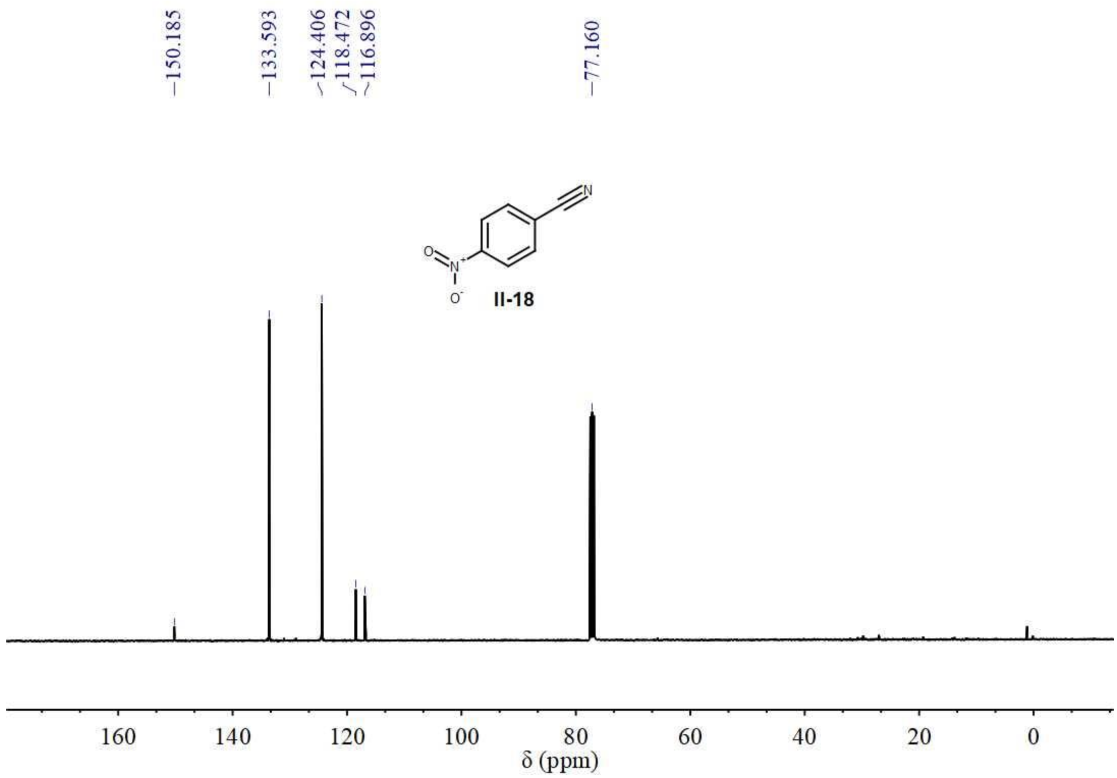
7.795
7.260
4.00
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

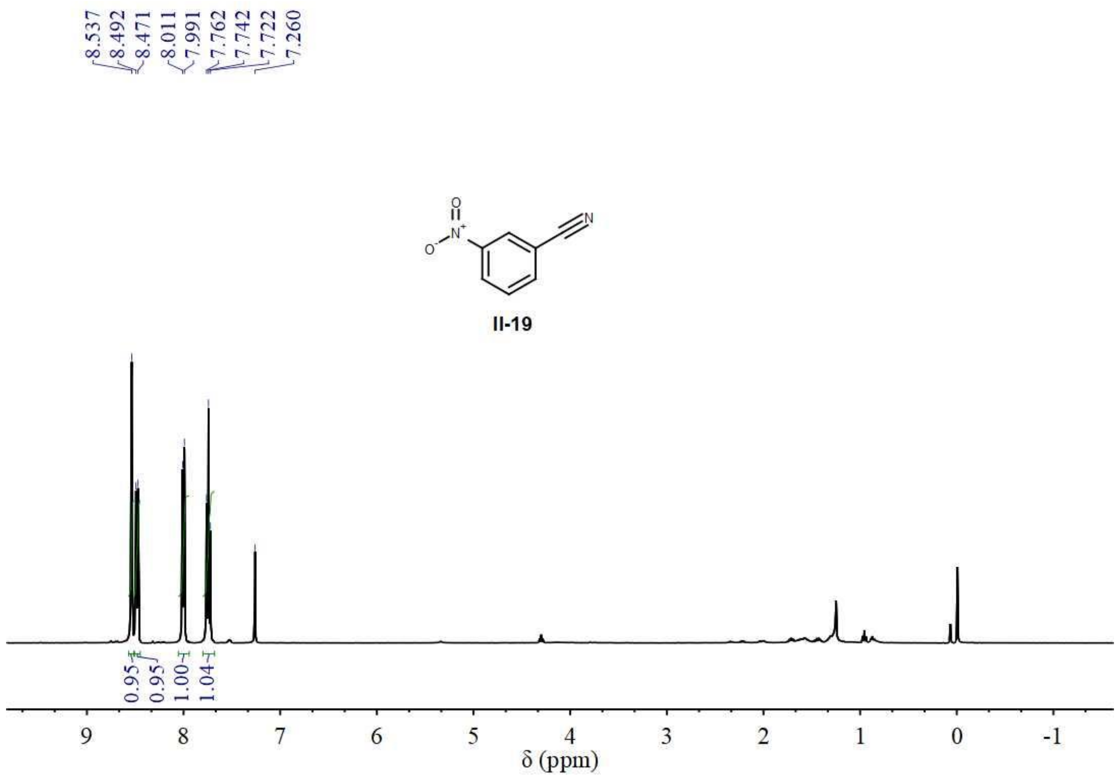


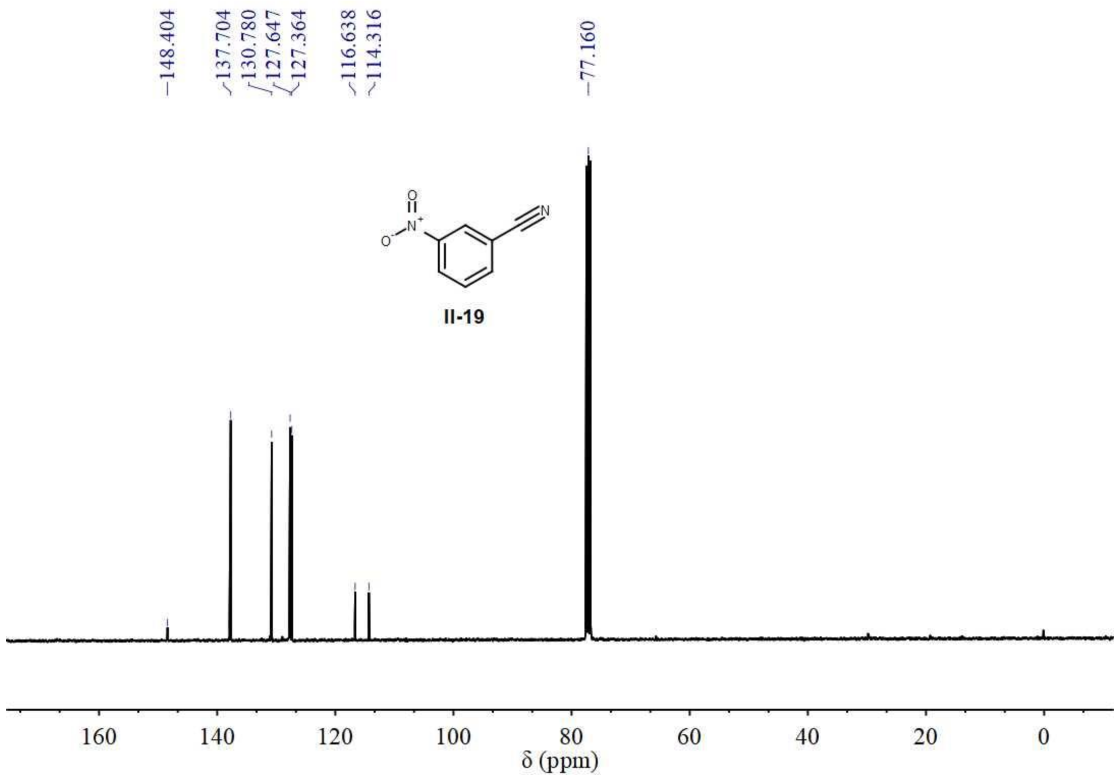
132.926
117.121
116.897
77.160
II-17
160 140 120 100 80 60 40 20 0
δ (ppm)

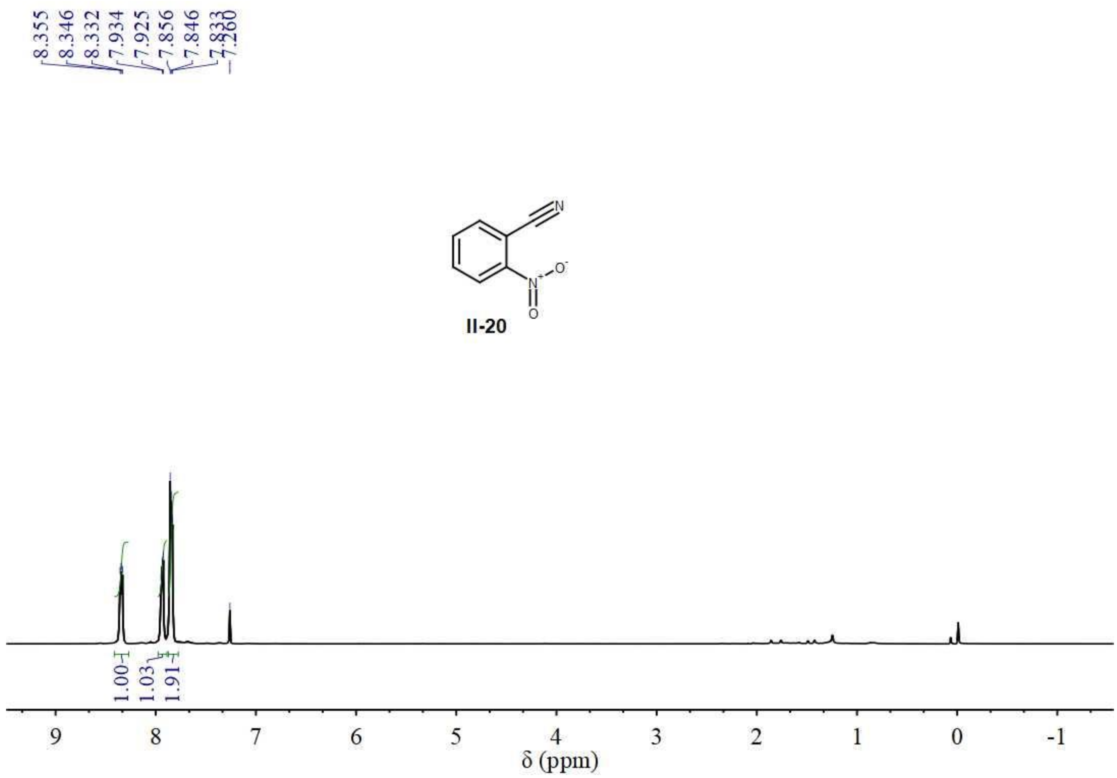


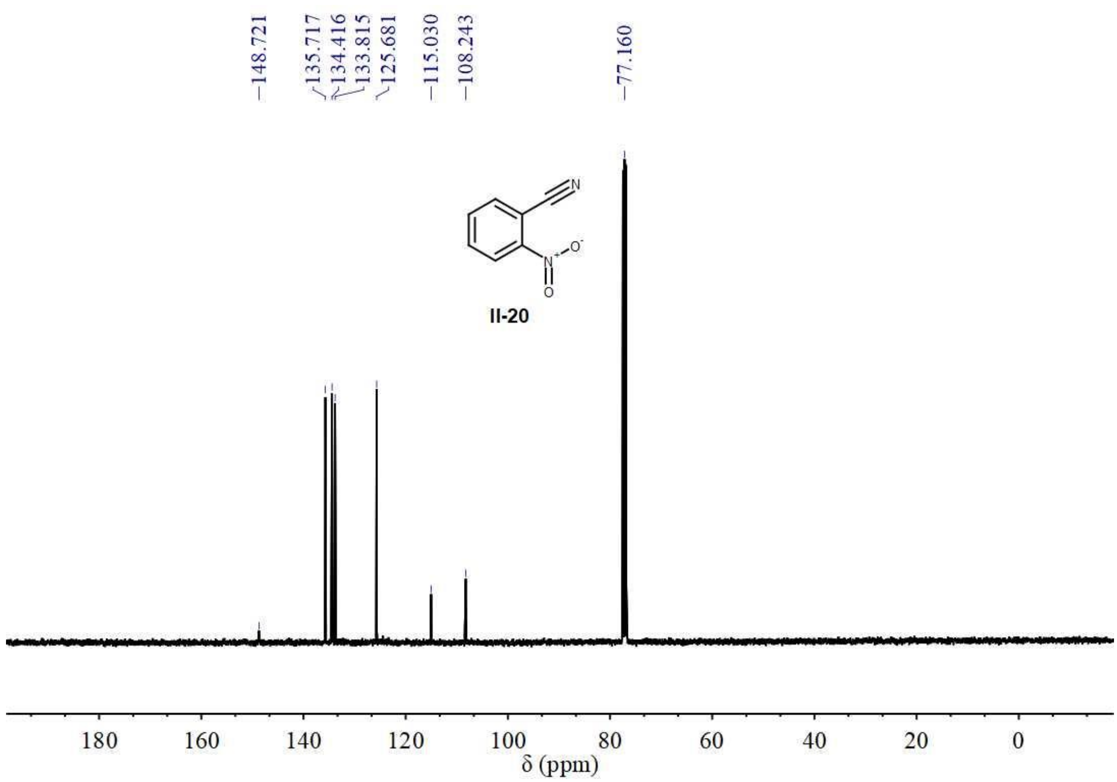
8.365
8.344
7.898
7.877
7.260
II-18
1.00
1.01
9 8 7 6 5 4 3 2 1 0 -1
δ (ppm)

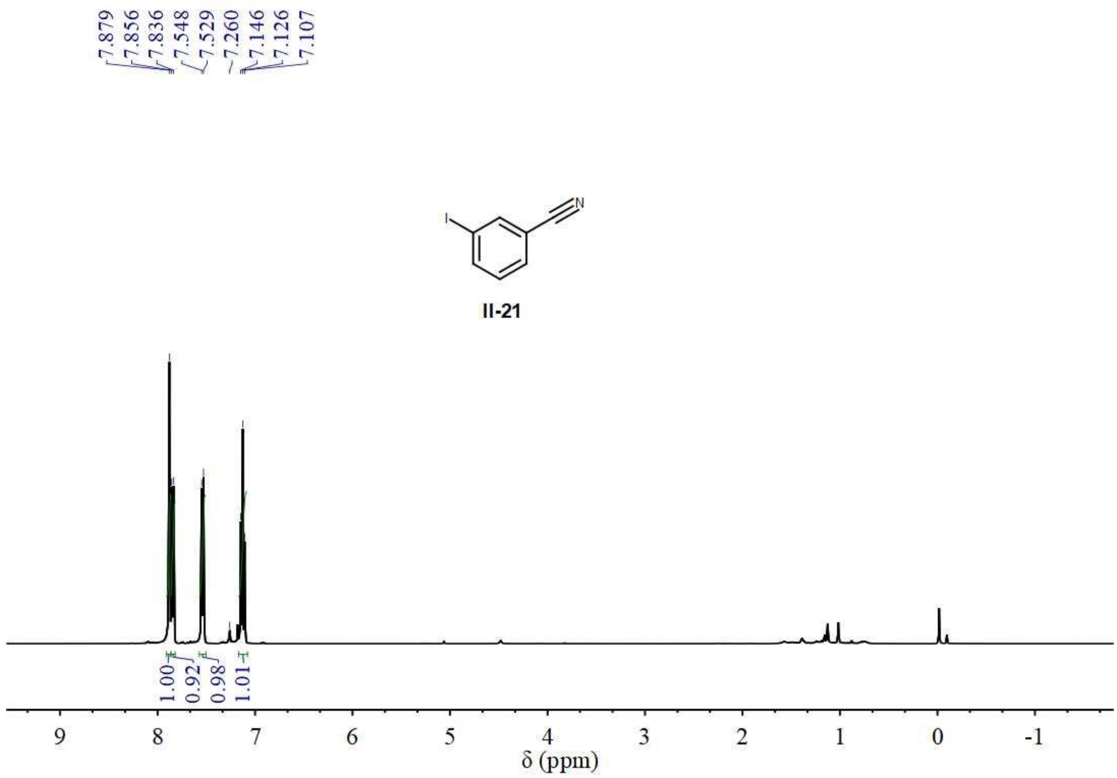

150.185
133.593
124.406
118.472
116.896
77.160
II-18
160
140
120
100
80
60
40
20
0
δ (ppm)

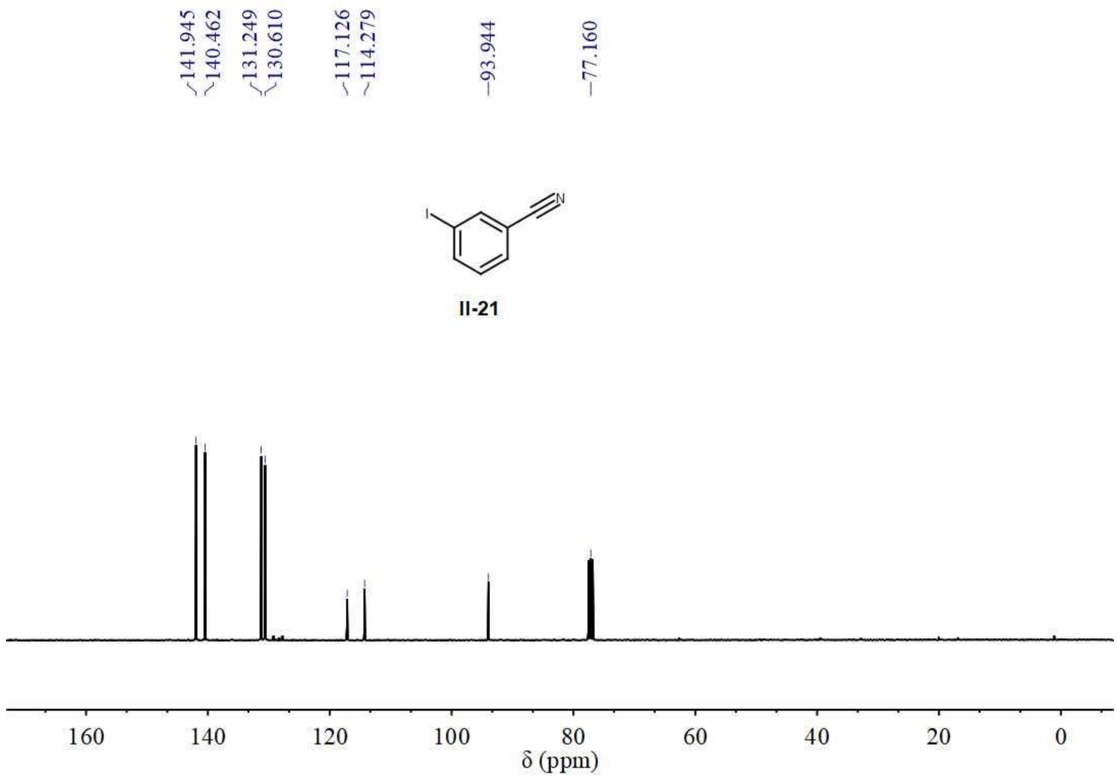

8.537
8.492
8.471
8.011
7.991
7.762
7.742
7.722
7.260
II-19
0.95
0.95
1.00
1.04
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

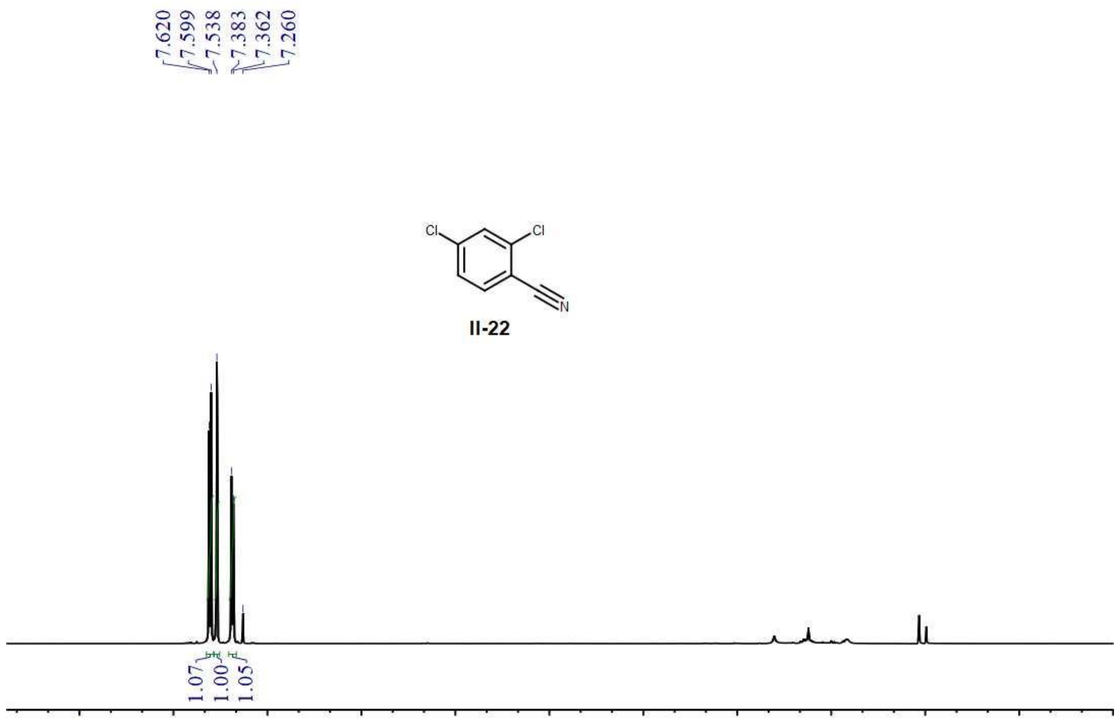

148.404
137.704
130.780
127.647
127.364
116.638
114.316
77.160
II-19
160
140
120
100
80
60
40
20
0
δ (ppm)

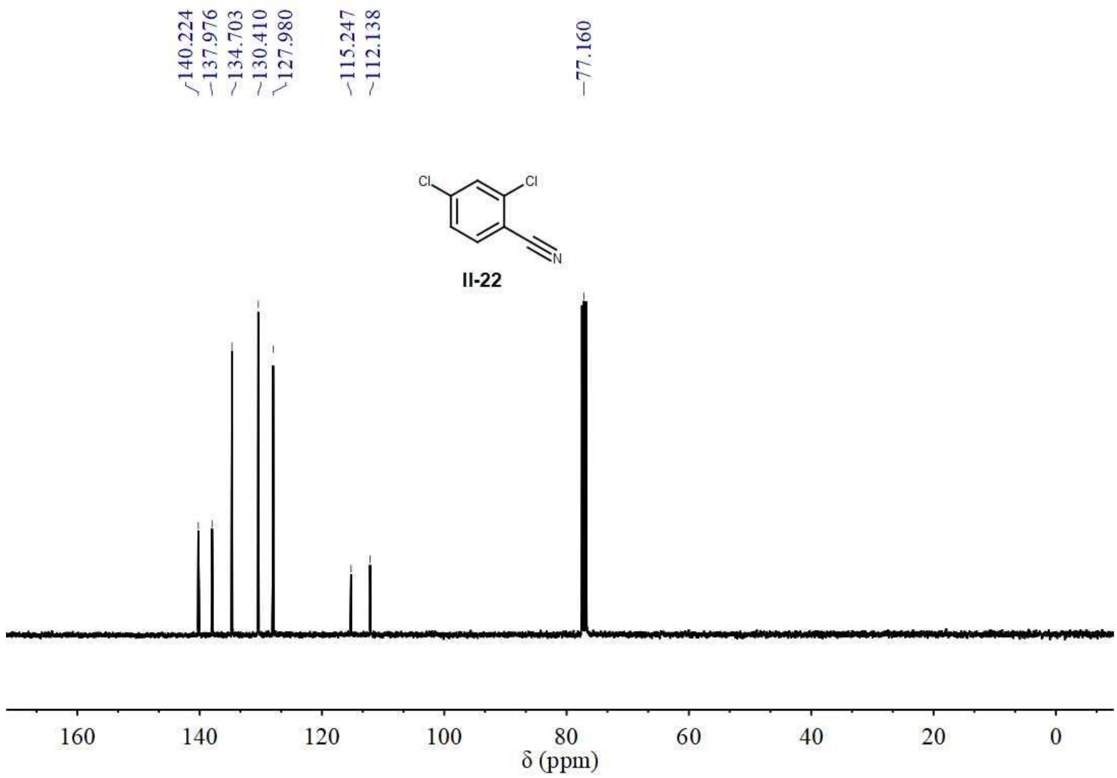

8.355
8.346
8.332
7.934
7.925
7.856
7.846
7.833
7.260
II-20
1.00
1.03
1.91
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

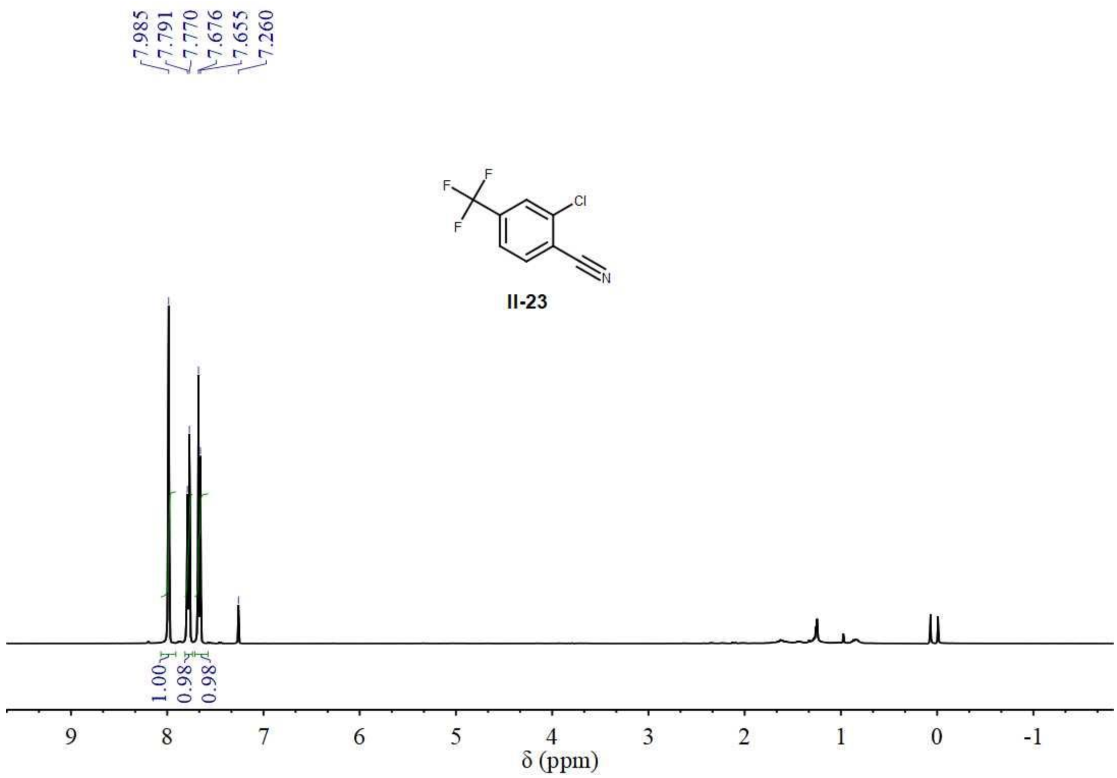

148.721
135.717
134.416
133.815
125.681
115.030
108.243
77.160
II-20
180 160 140 120 100 80 60 40 20 0
δ (ppm)

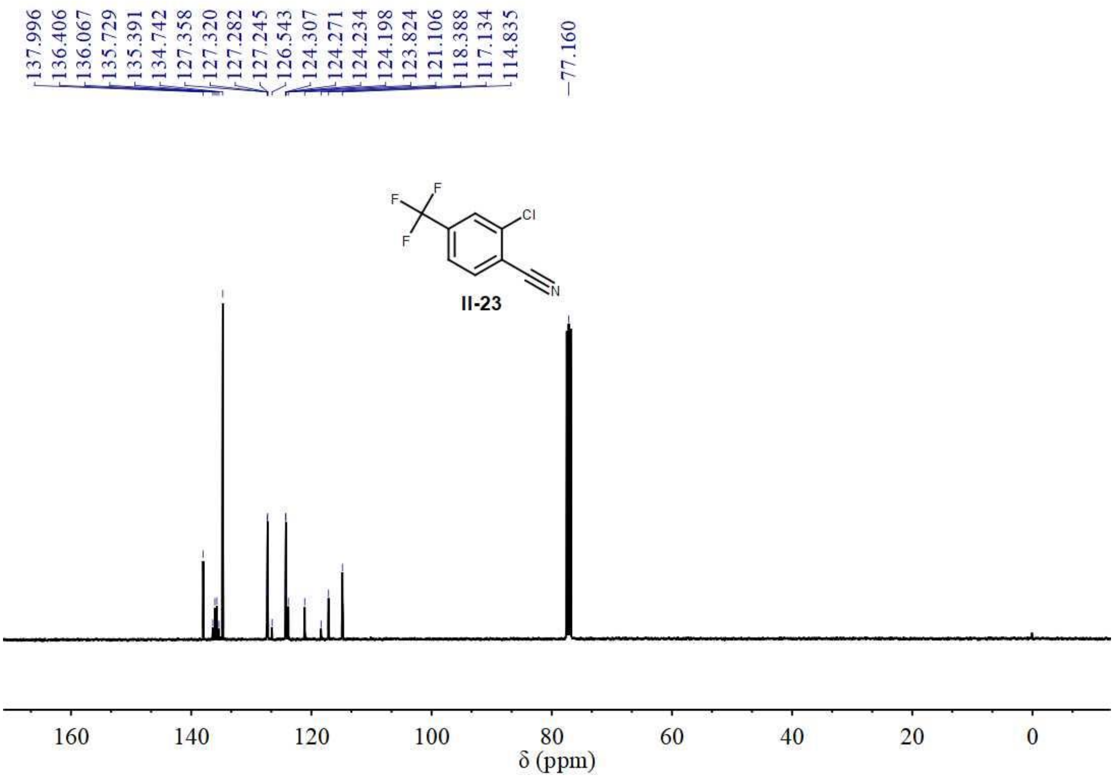

7.879
7.856
7.836
7.548
7.529
7.260
7.146
7.126
7.107
II-21
1.00
0.92
0.98
1.01
9 8 7 6 5 4 3 2 1 0 -1
δ (ppm)

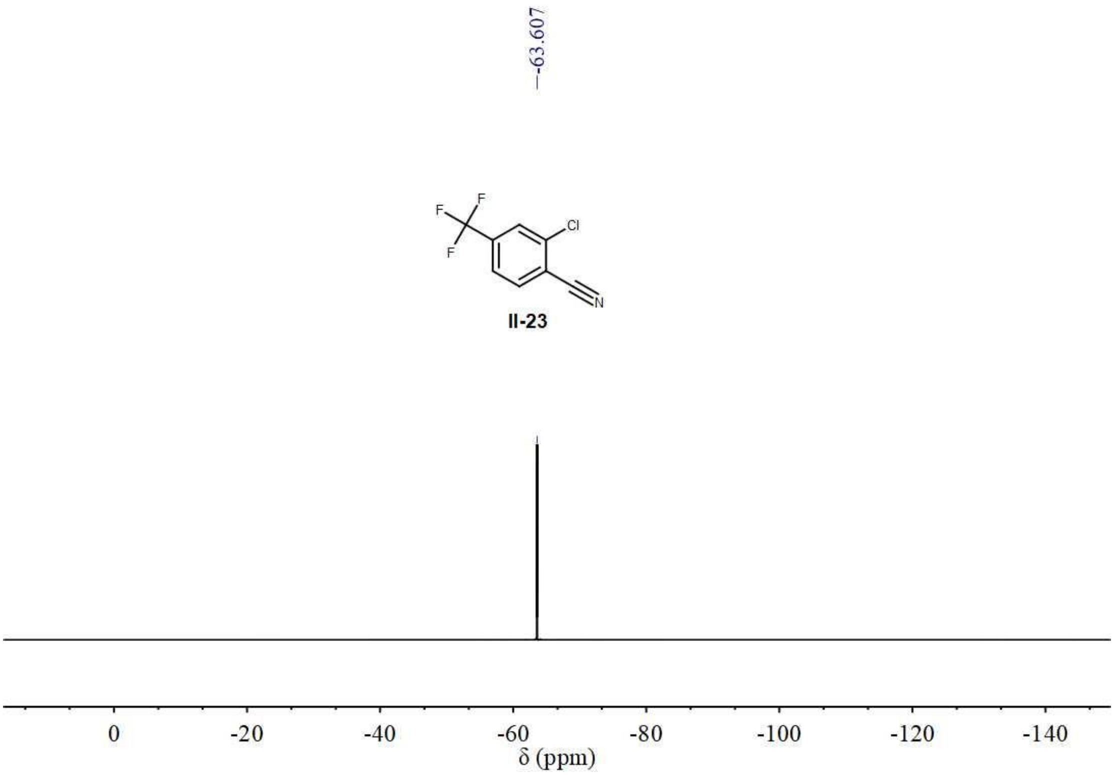

141.945
140.462
131.249
130.610
117.126
114.279
93.944
77.160
I
N
II-21
160
140
120
100
80
60
40
20
0
δ (ppm)

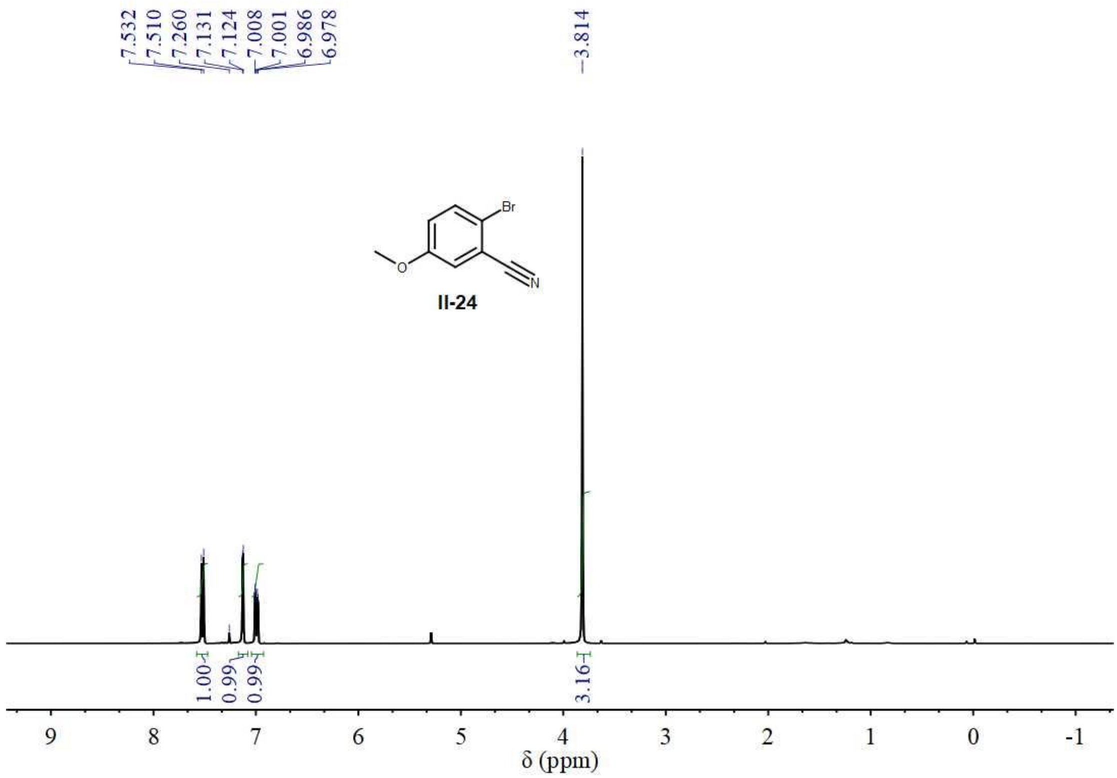

7.620
7.599
7.538
7.383
7.362
7.260
Cl
Cl
N
II-22
1.07
1.00
1.05
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

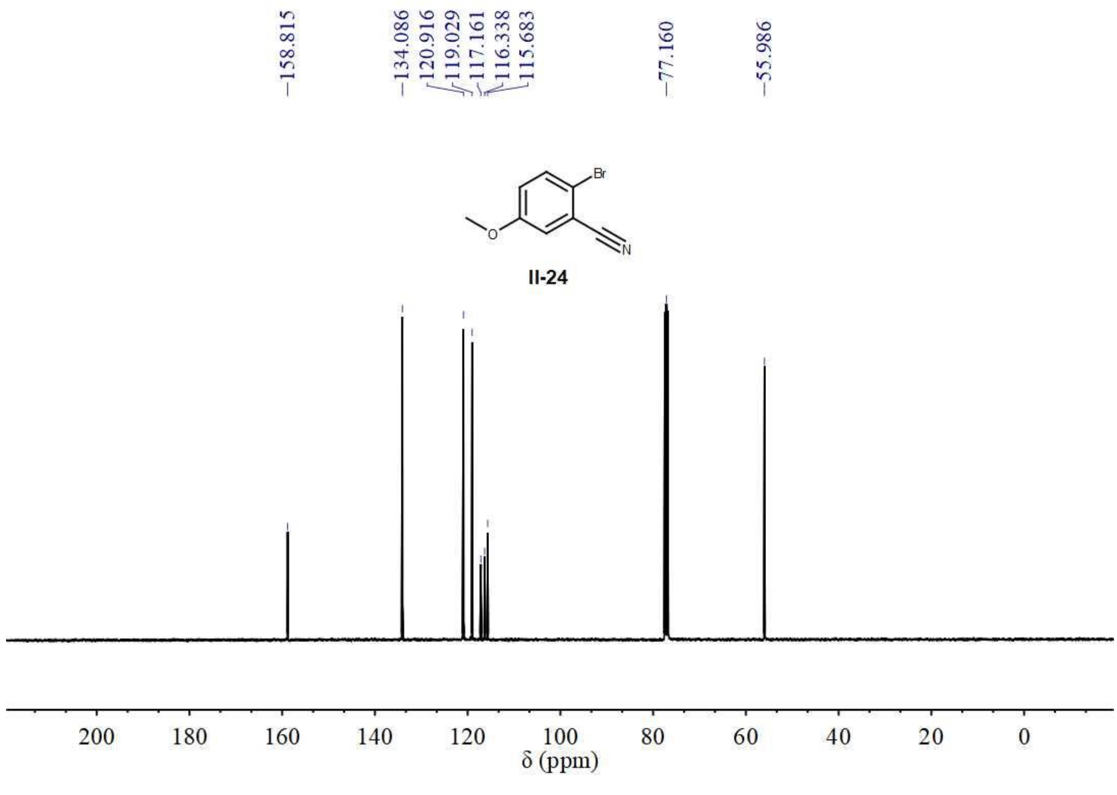

140.224
137.976
134.703
130.410
127.980
115.247
112.138
77.160
Cl
Cl
N
II-22
160
140
120
100
80
60
40
20
0
δ (ppm)

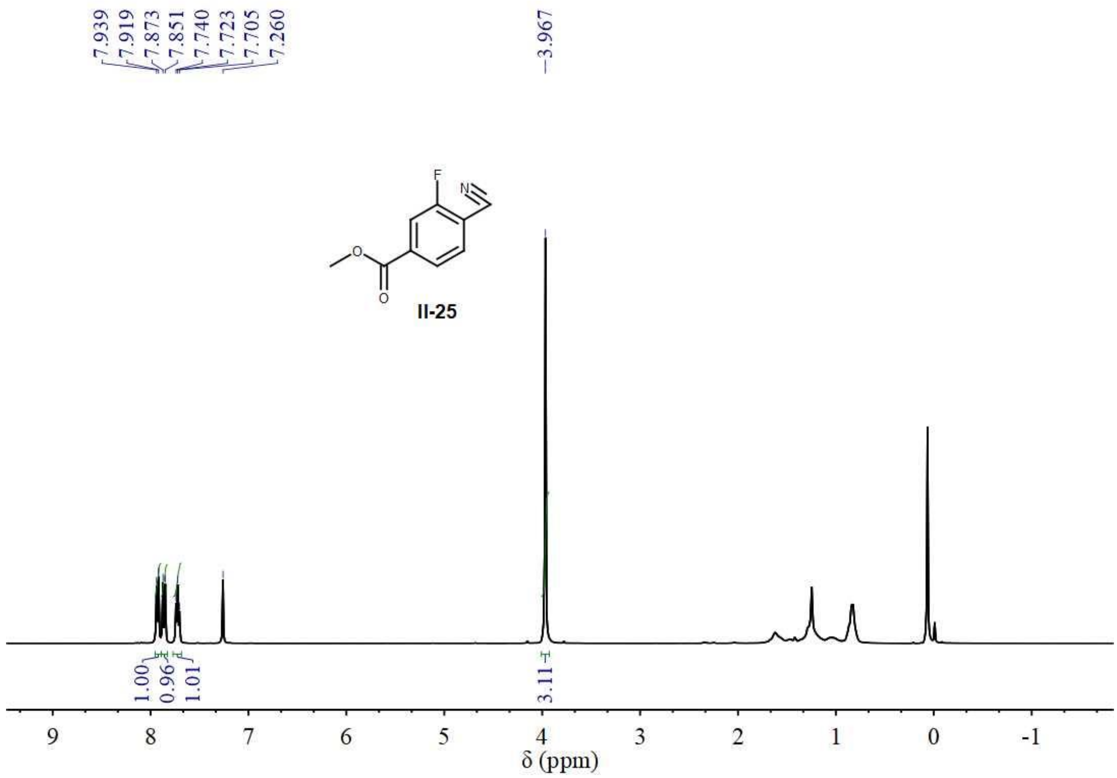

7.985
7.791
7.770
7.676
7.655
7.260
F
F
F
Cl
N
II-23
1.00
0.98
0.98
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

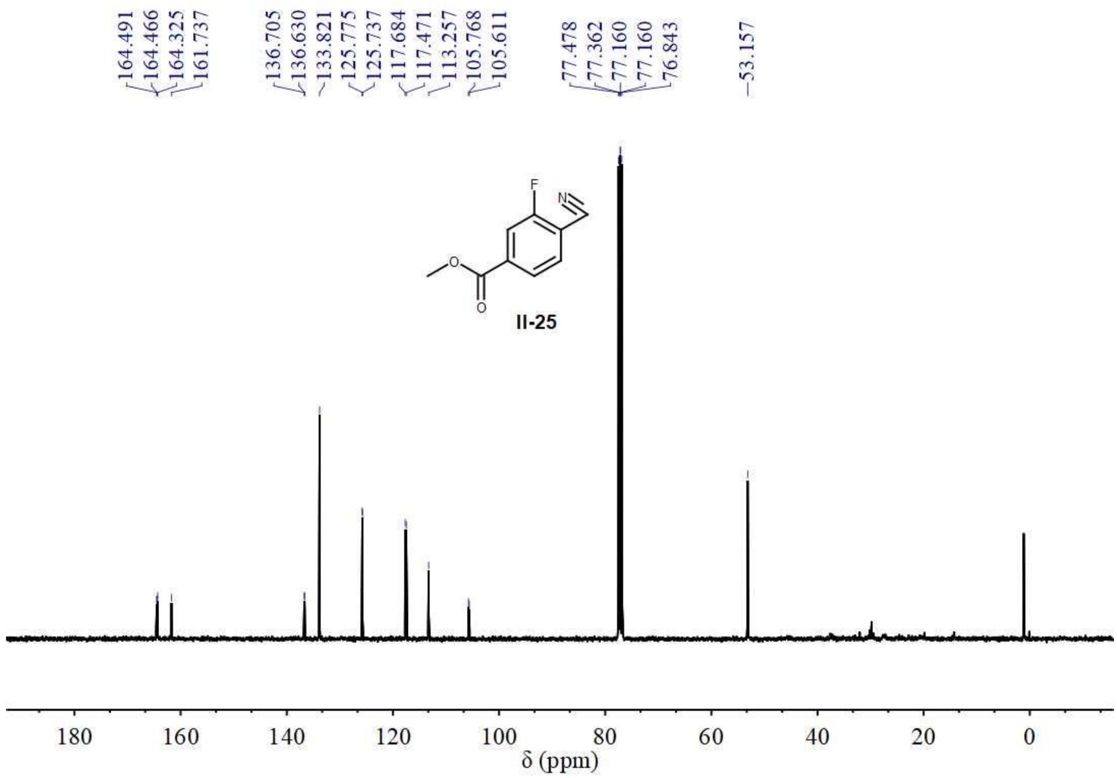

137.996
136.406
136.067
135.729
135.391
134.742
127.358
127.320
127.282
127.245
126.543
124.307
124.271
124.234
124.198
123.824
121.106
118.388
117.134
114.835
77.160
F
F
F
Cl
N
II-23
160
140
120
100
80
60
40
20
0
δ (ppm)

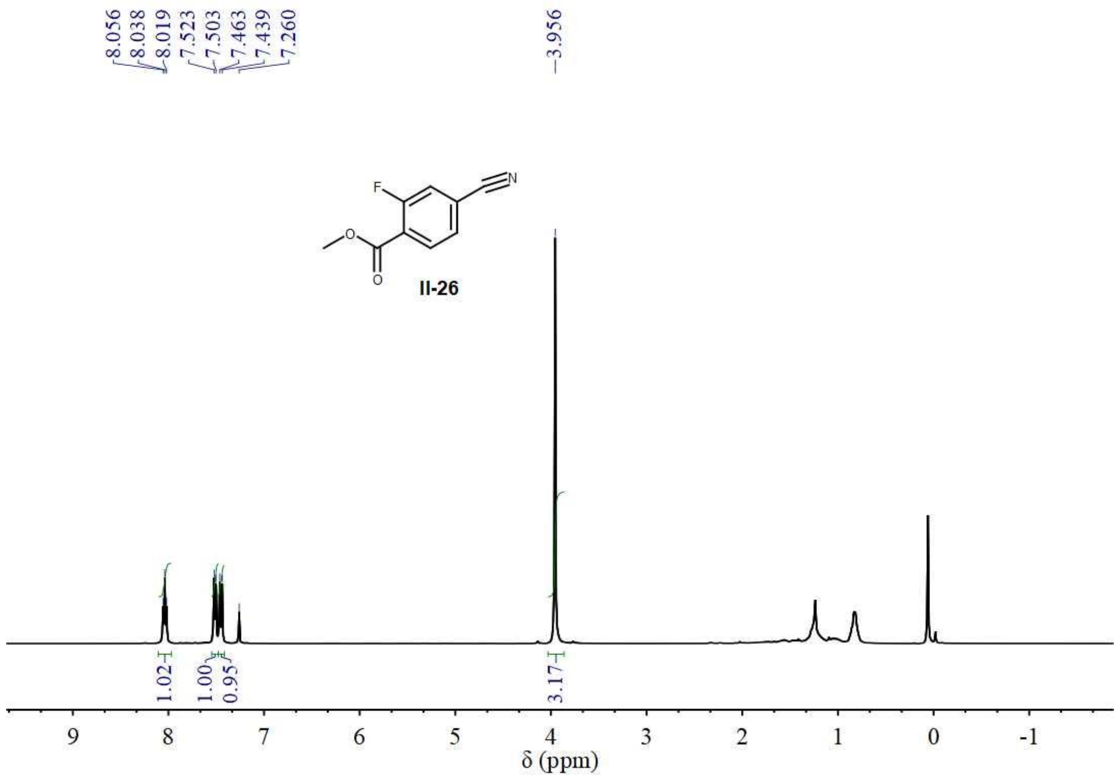

-63.607
F
F
F
Cl
N
II-23
0
-20
-40
-60
-80
-100
-120
-140
δ (ppm)


7.532
7.510
7.260
7.131
7.124
7.008
7.001
6.986
6.978
3.814
Br
O
N
II-24
1.00
0.99
0.99
3.16
9 8 7 6 5 4 3 2 1 0 -1
δ (ppm)


158.815
134.086
120.916
119.029
117.161
116.338
115.683
77.160
55.986
Br
O
N
II-24
200 180 160 140 120 100 80 60 40 20 0
δ (ppm)

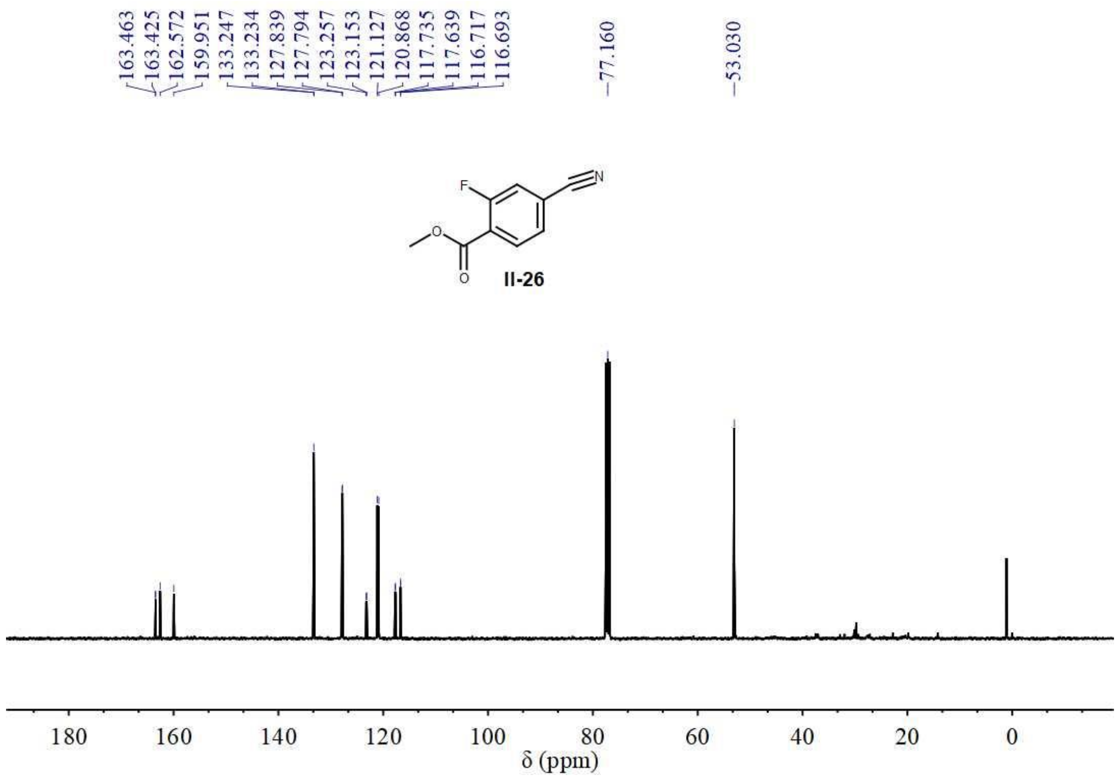

7.939
7.919
7.873
7.851
7.740
7.723
7.705
7.260
3.967
F
N
O
O
II-25
1.00
0.96
1.01
3.11
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)


164.491
164.466
164.325
161.737
136.705
136.630
133.821
125.775
125.737
117.684
117.471
113.257
105.768
105.611
77.478
77.362
77.160
77.160
76.843
53.157
F
N
O
O
II-25
180
160
140
120
100
80
60
40
20
0
δ (ppm)



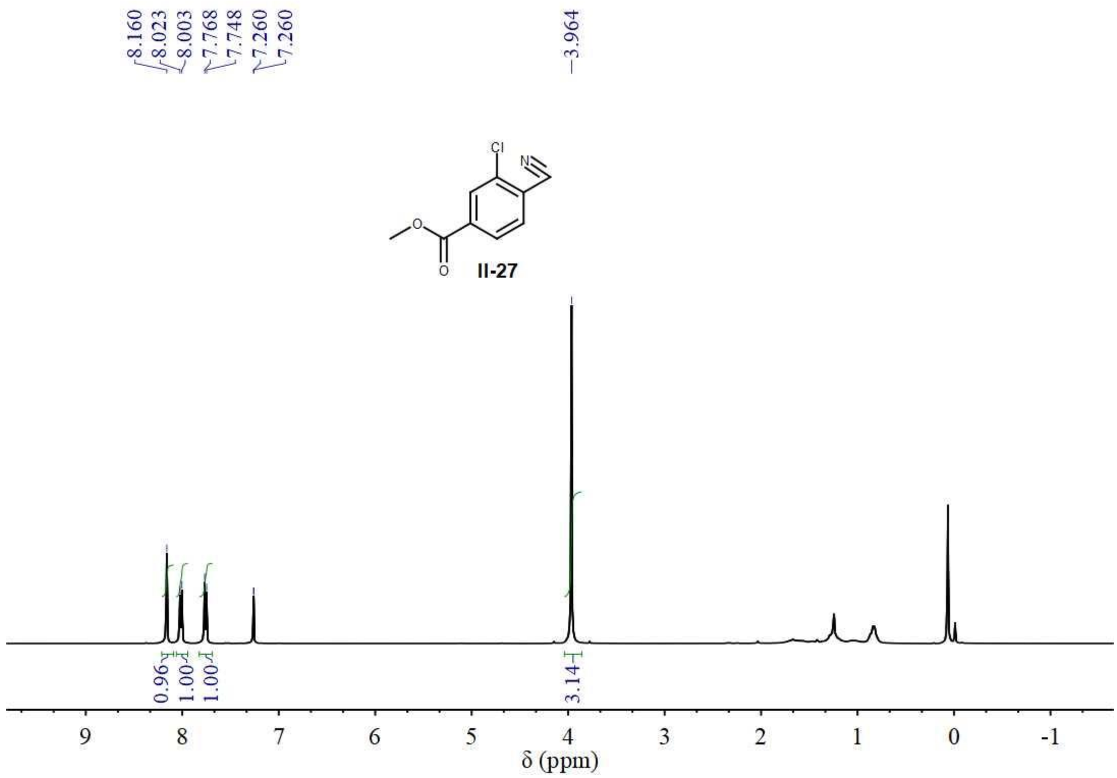
8.056
8.038
8.019
7.523
7.503
7.463
7.439
7.260
3.956
F
N
O
O
1.02
1.00
0.95
3.17
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

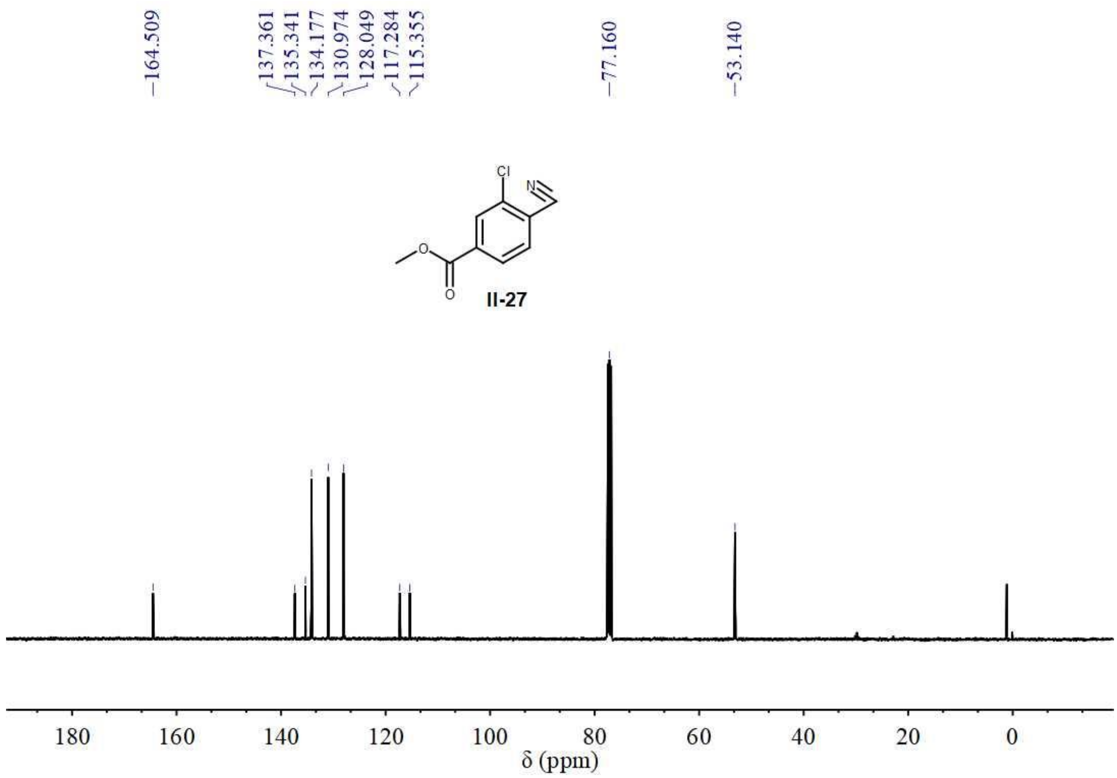
II-26



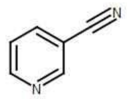
163.463
163.425
162.572
159.951
133.247
133.234
127.839
127.794
123.257
123.153
121.127
120.868
117.735
117.639
116.717
116.693
77.160
53.030
F
N
O
O
180
160
140
120
100
80
60
40
20
0
δ (ppm)

II-26

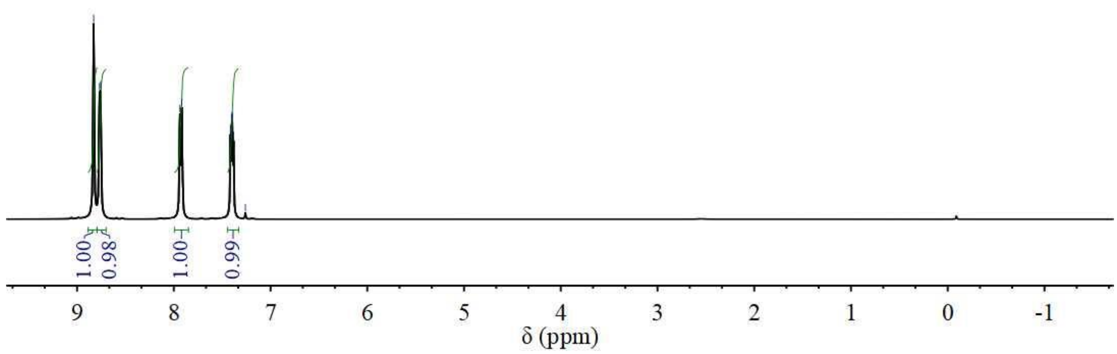

8.160
8.023
8.003
7.768
7.748
7.260
7.260
3.964
Cl
N
O
O
II-27
0.96
1.00
1.00
3.14
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)


164.509
137.361
135.341
134.177
130.974
128.049
117.284
115.355
77.160
53.140
Cl
N
O
O
II-27
180
160
140
120
100
80
60
40
20
0
δ (ppm)

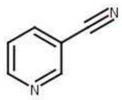
8.828
8.768
8.756
7.937
7.917
7.415
7.401
7.398
7.395
7.383
7.260



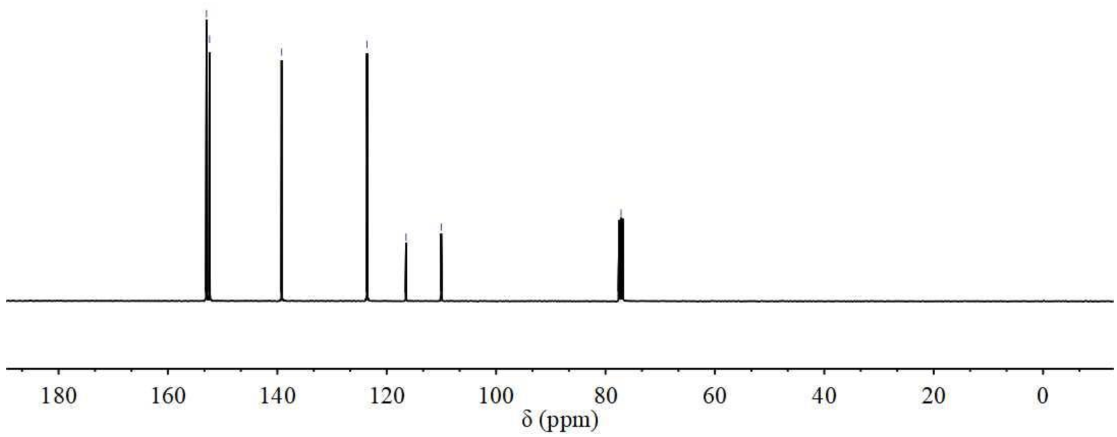
II-28

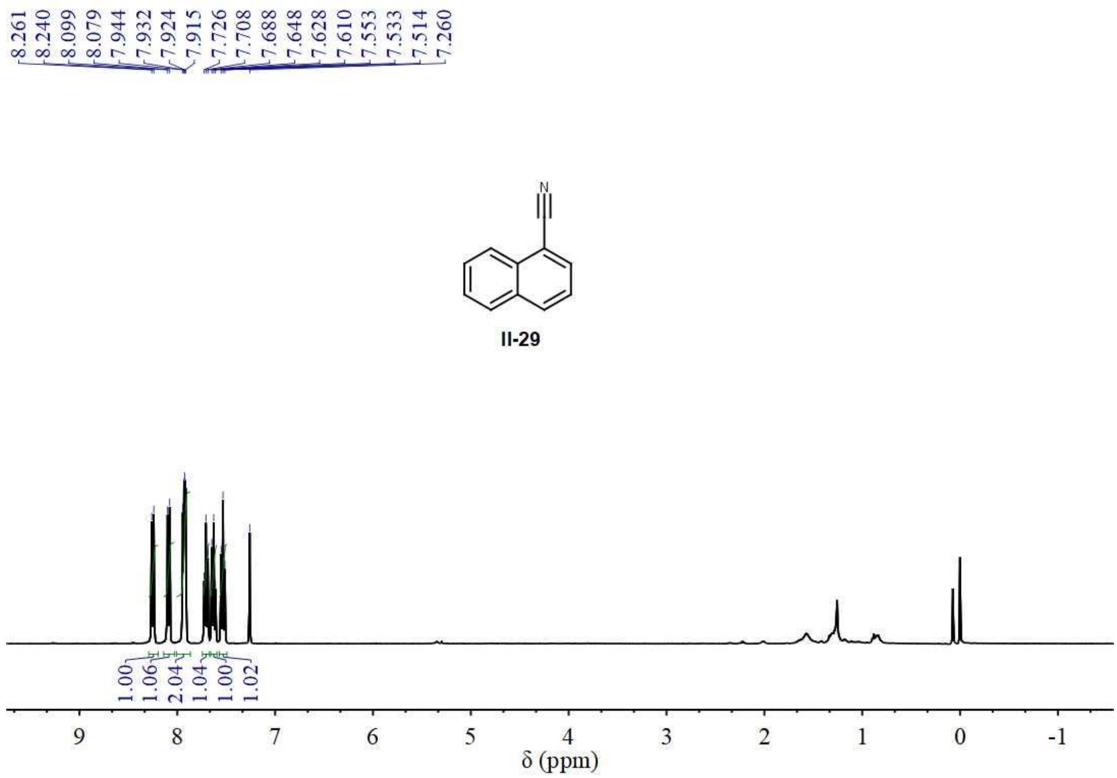

1.00
0.98
1.00
0.99
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

152.948
152.391
139.207
123.598
116.461
110.044
77.160

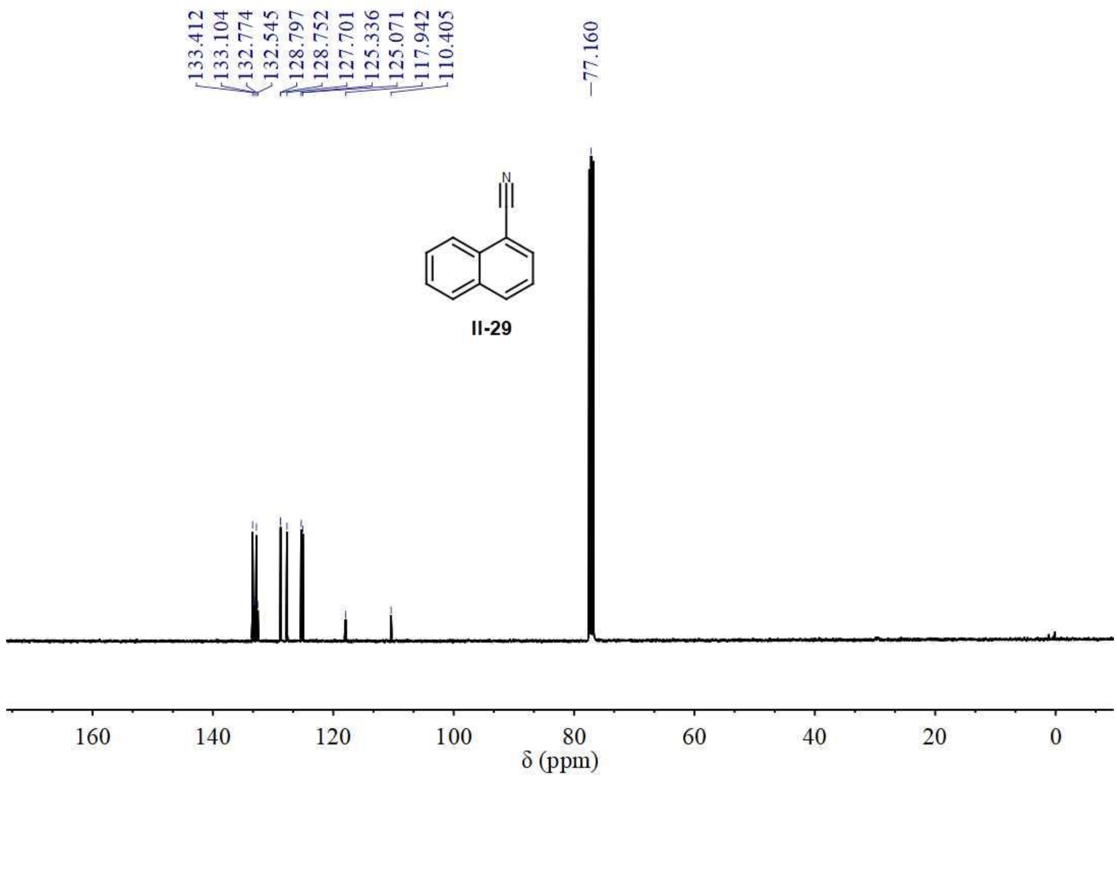


II-28

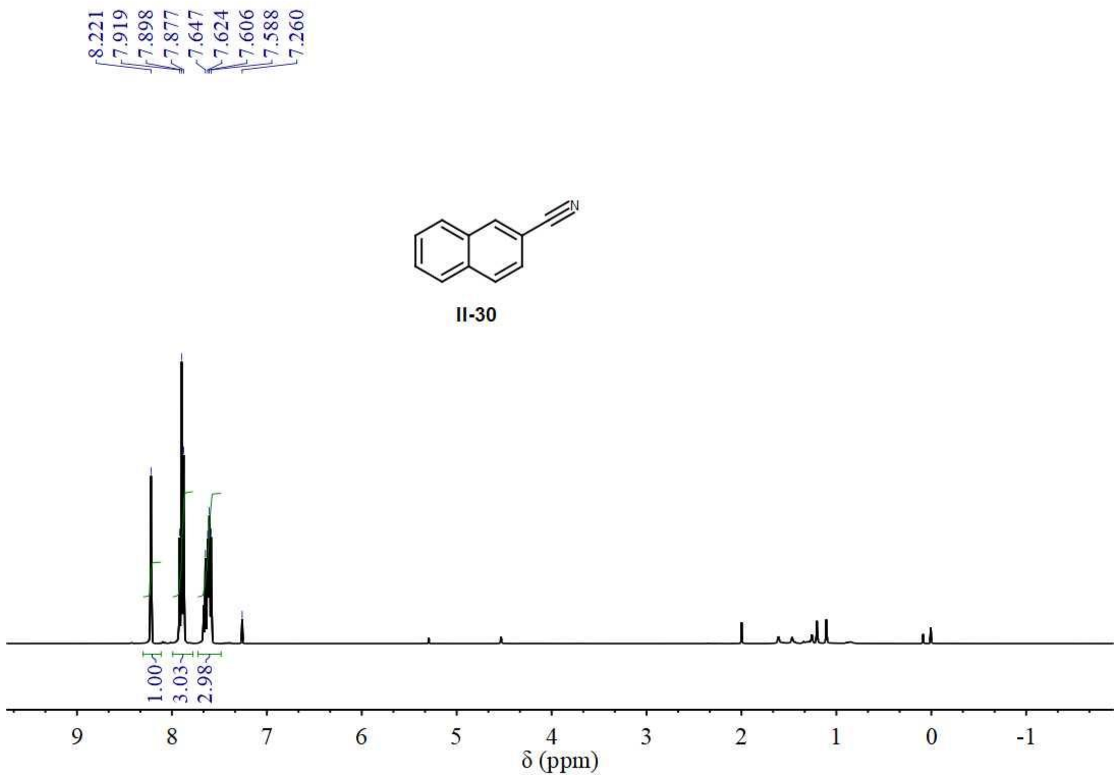

180
160
140
120
100
80
60
40
20
0
δ (ppm)

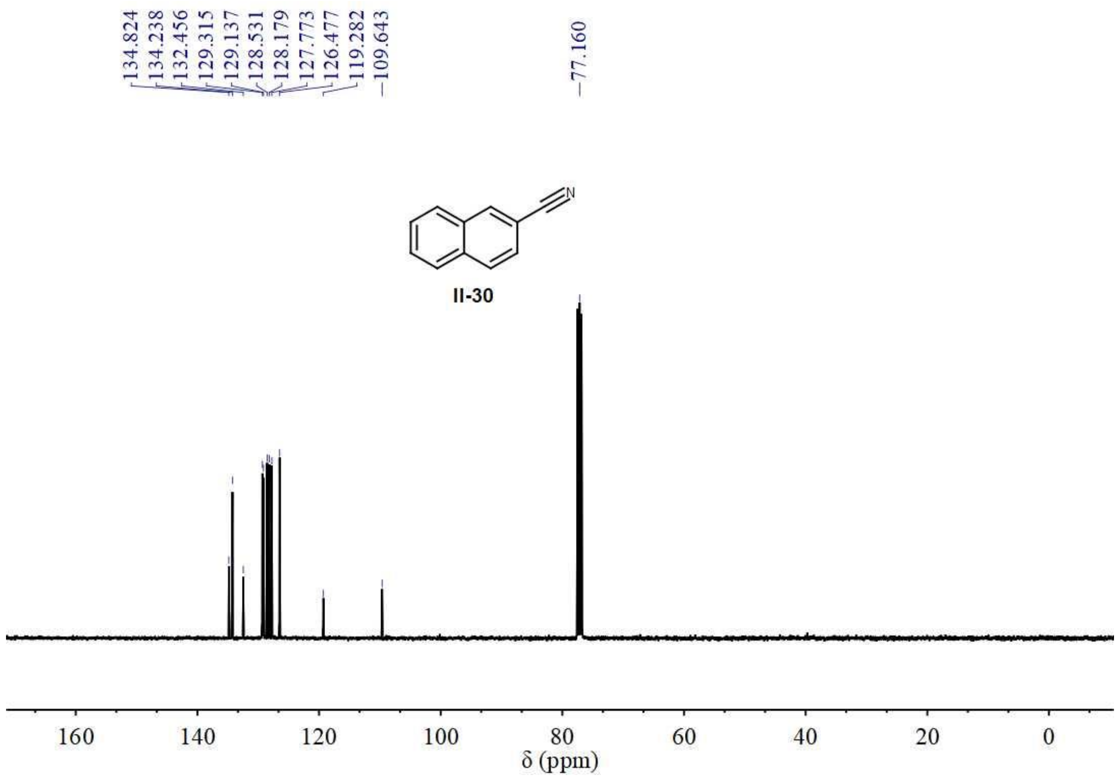

8.261
8.240
8.099
8.079
7.944
7.932
7.924
7.915
7.726
7.708
7.688
7.648
7.628
7.610
7.553
7.533
7.514
7.260
N
1.00
1.06
2.04
1.04
1.00
1.02
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

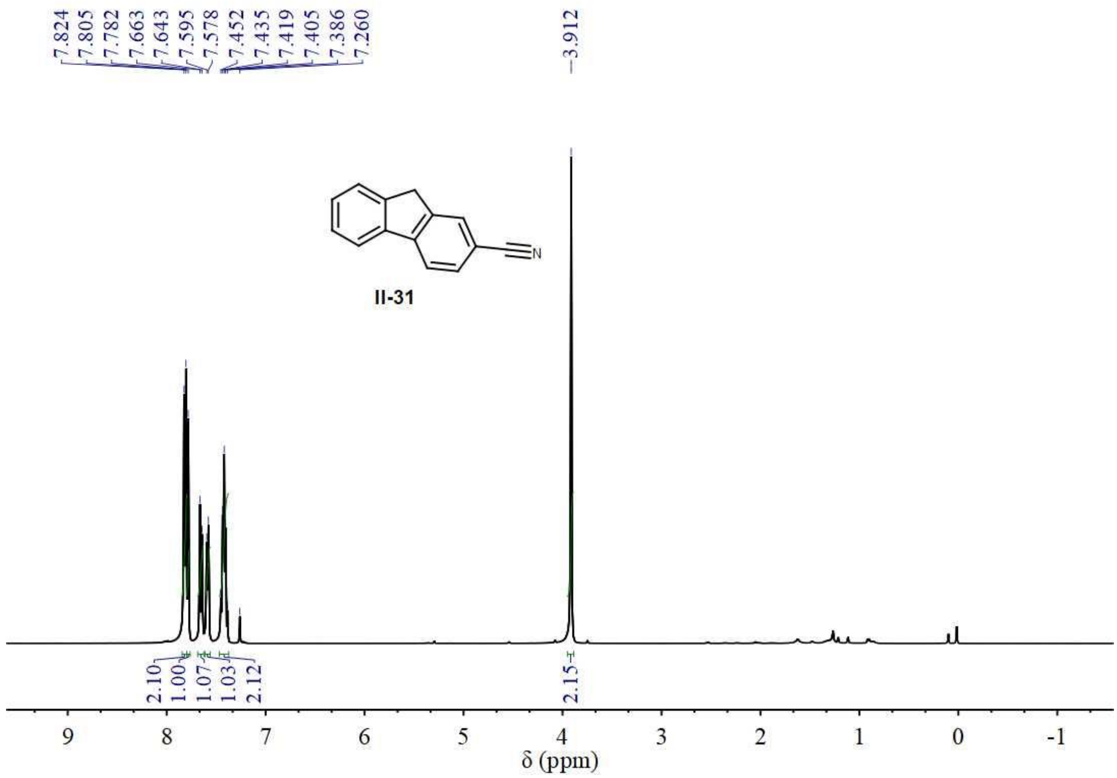
II-29

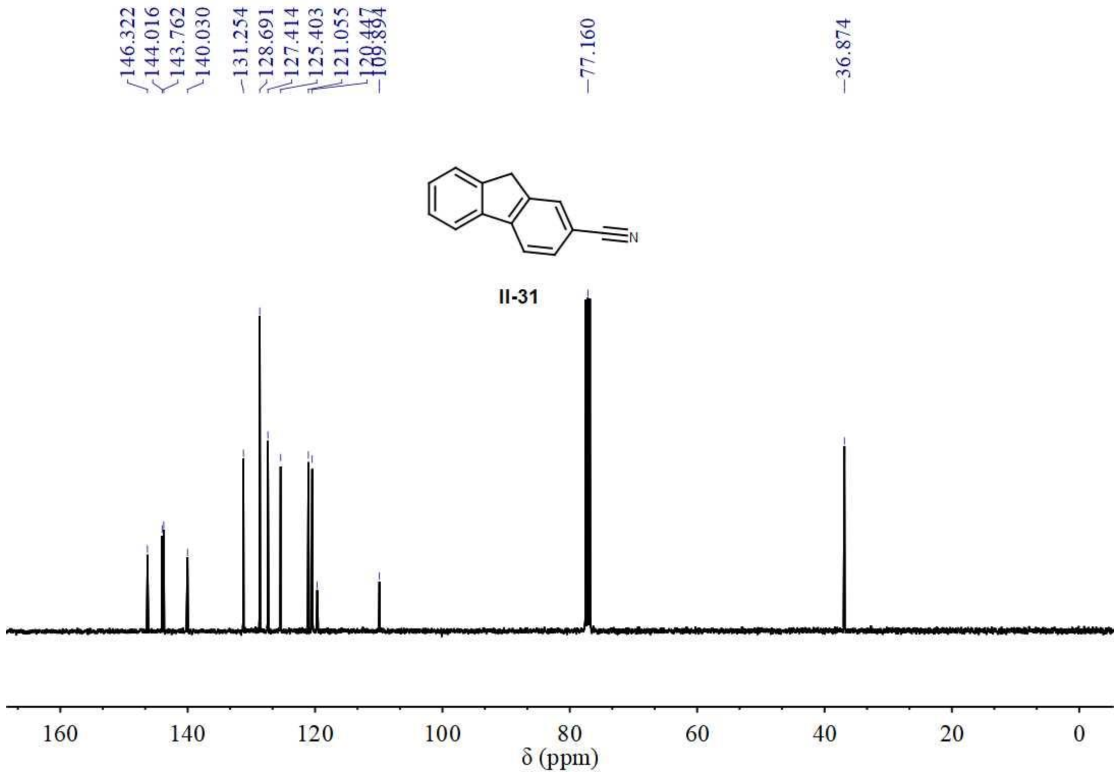

133.412
133.104
132.774
132.545
128.797
128.752
127.701
125.336
125.071
117.942
110.405
77.160
N
160
140
120
100
80
60
40
20
0
δ (ppm)

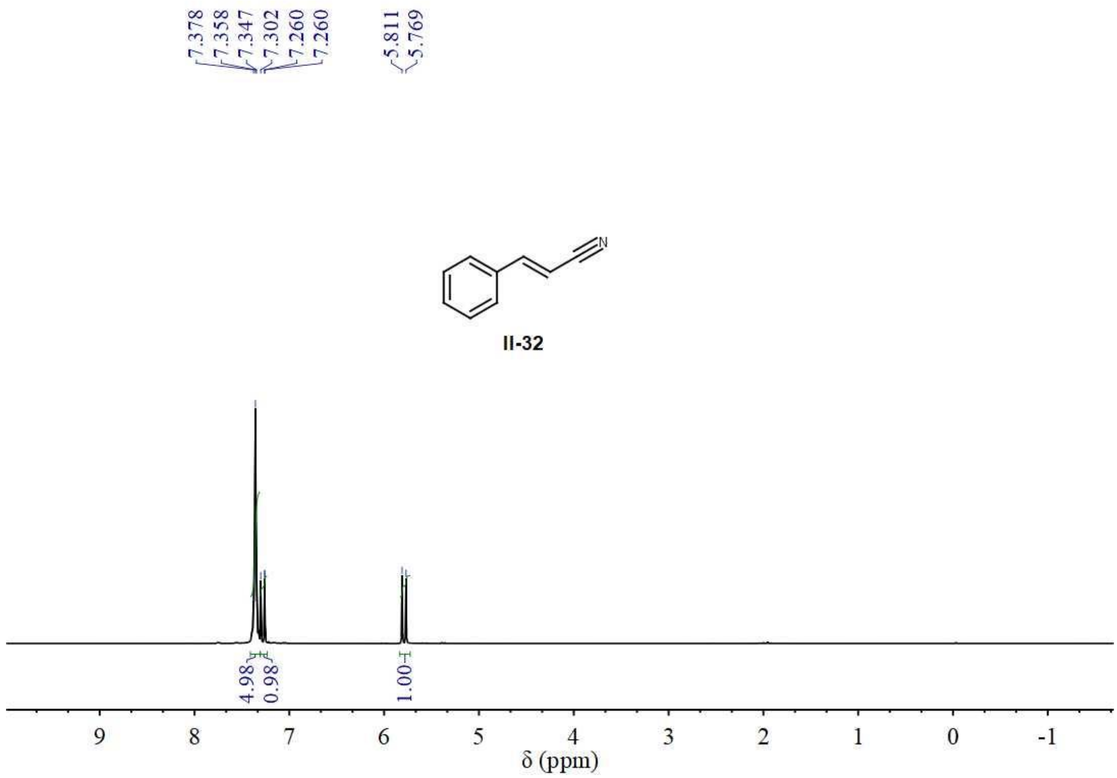
II-29

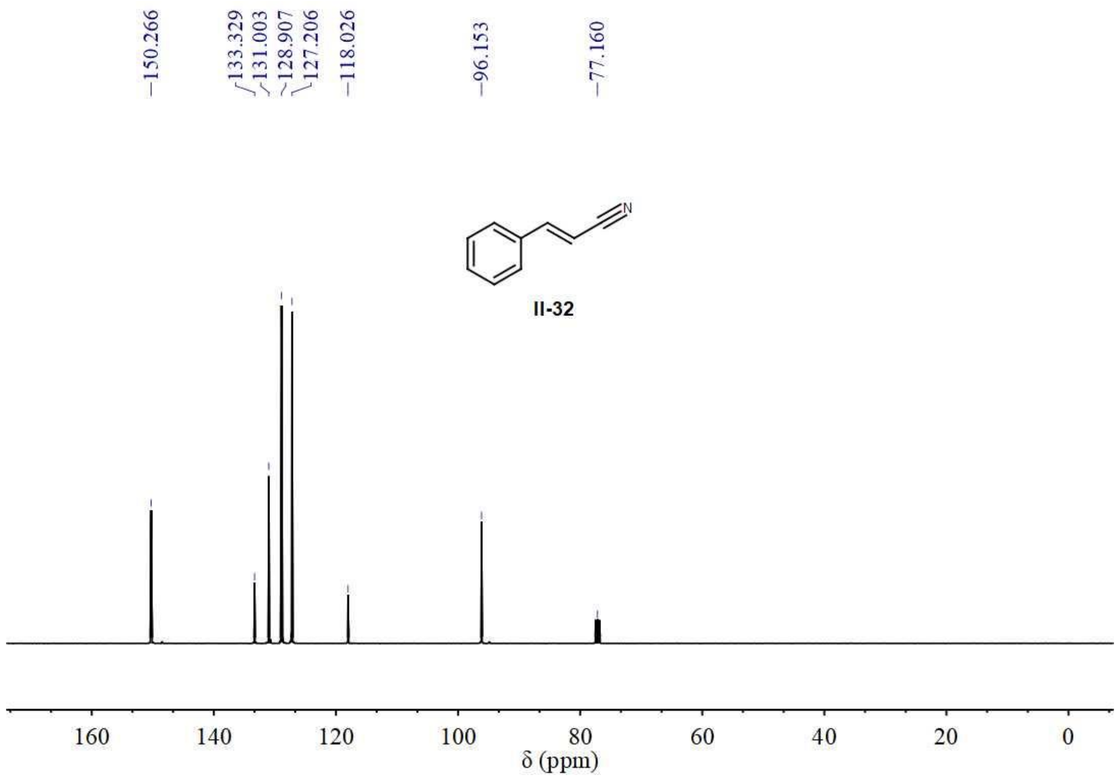

8.221
7.919
7.898
7.877
7.647
7.624
7.606
7.588
7.260
N
II-30
1.00
3.03
2.98
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

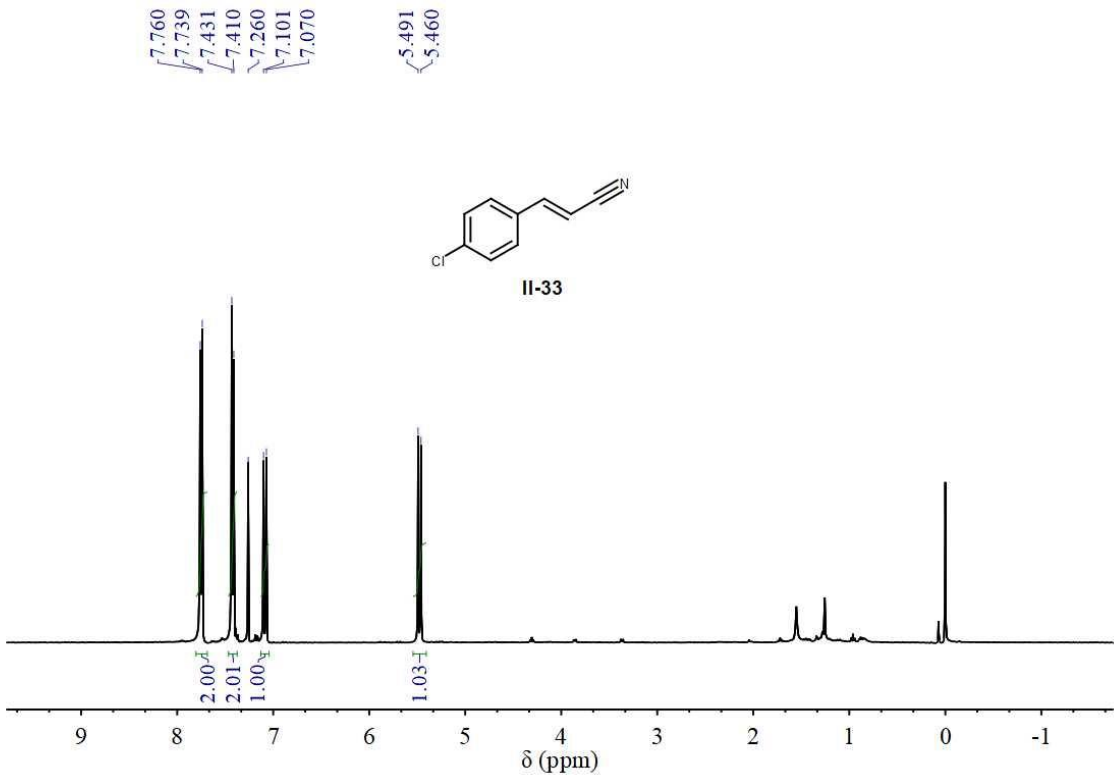

134.824
134.238
132.456
129.315
129.137
128.531
128.179
127.773
126.477
119.282
109.643
77.160
N
II-30
160
140
120
100
80
60
40
20
0
δ (ppm)

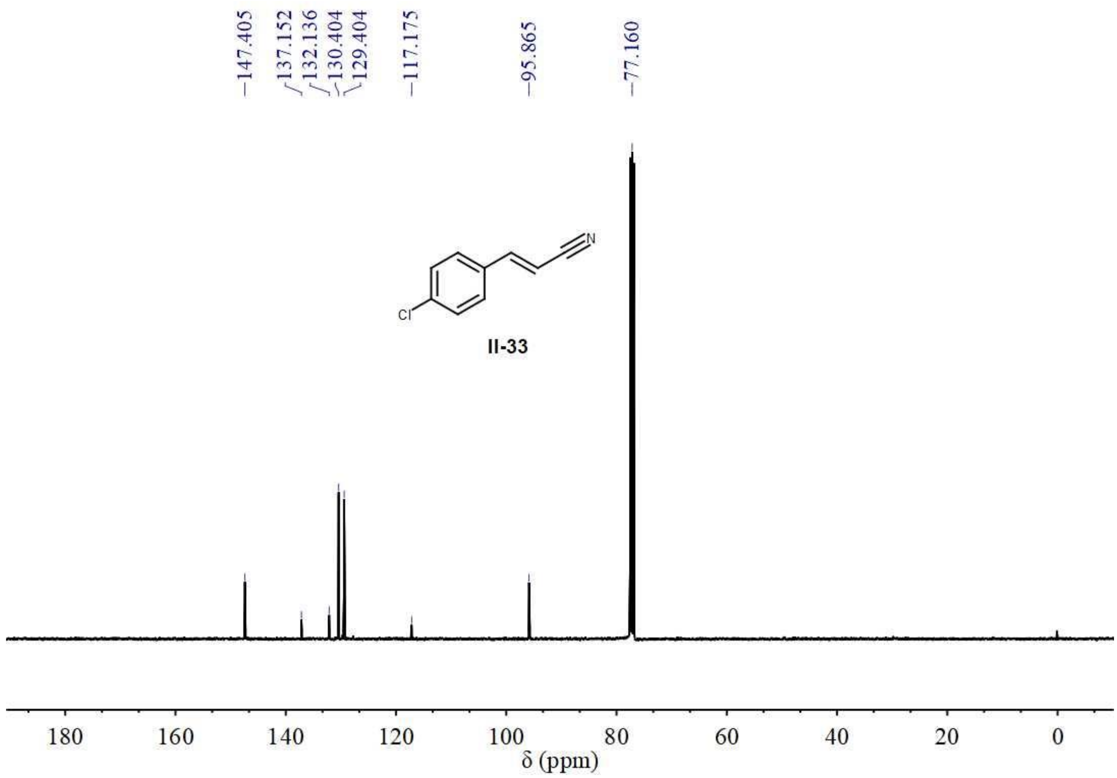

7.824
7.805
7.782
7.663
7.643
7.595
7.578
7.452
7.435
7.419
7.405
7.386
7.260
3.912
II-31
2.10
1.00
1.07
1.03
2.12
2.15
δ (ppm)

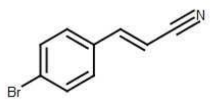

146.322
144.016
143.762
140.030
131.254
128.691
127.414
125.403
121.055
120.447
109.894
77.160
36.874
II-31
δ (ppm)


7.378
7.358
7.347
7.302
7.260
7.260
5.811
5.769
N
II-32
4.98
0.98
1.00
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

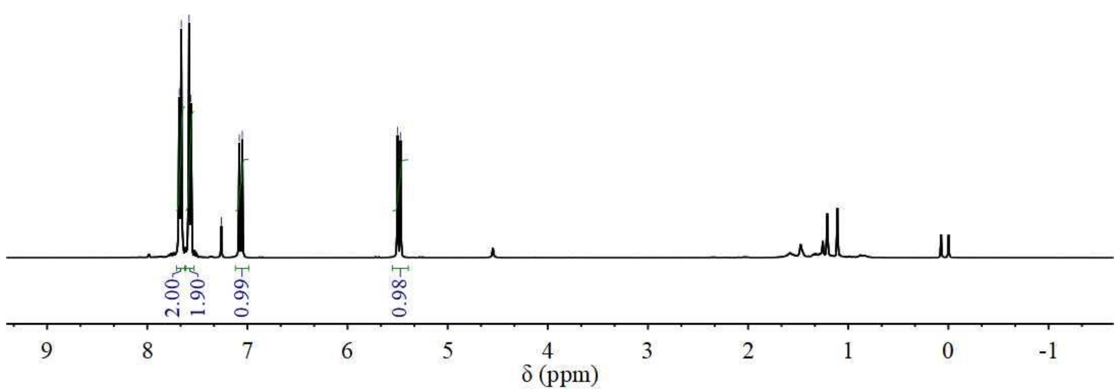

150.266
133.329
131.003
128.907
127.206
118.026
96.153
77.160
N
II-32
160
140
120
100
80
60
40
20
0
δ (ppm)

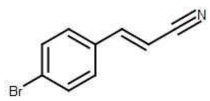

7.760
7.739
7.431
7.410
7.260
7.101
7.070
5.491
5.460
Cl
N
II-33
2.00
2.01
1.00
1.03
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)


147.405
137.152
132.136
130.404
129.404
117.175
95.865
77.160
Cl
N
II-33
180
160
140
120
100
80
60
40
20
0
δ (ppm)

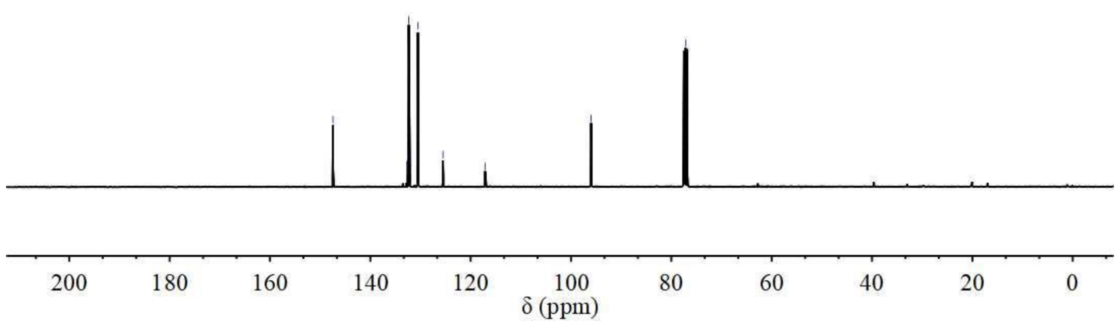


II-34


7.680
7.660
7.583
7.563
7.260
7.260
7.082
7.051
5.500
5.470
2.00
1.90
0.99
0.98
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)



II-34


147.456
132.511
132.338
130.513
125.514
117.118
95.989
77.160
200
180
160
140
120
100
80
60
40
20
0
δ (ppm)